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CHEMICAL CHARACTERIZATION OF THE POLYNUCLEAR AROMATIC HYDROCARBONS IN FRACTIONS BOILING ABOVE 350°C

for

Department of Energy, Mines and Resources
CANMET, Energy Research Laboratories
555 Booth Street
Ottawa, Ontario
K1A 0G1

Attention: Dr. M.A. Poirier

Work carried out jointly between United Technology and Science, Inc. (UTS) and Ontario Research Foundation (ORF)
(Principal Investigator: Dr. B.S. Das)

by

B.S. Das, Ph.D.
Ontario Research Foundation
Sheridan Park Research Community
Mississauga, Ontario L5K 1B3

and

D. Kane, Ph.D.
United Technology and Science, Inc.
75 Eglinton Avenue East
Toronto, Ontario M4P 1H3

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EXECUTIVE SUMMARY

This work, conducted jointly by United Technology and Science, Inc. (UTS) and the Ontario Research Foundation (ORF), describes the separation and characterization by instrumental analysis techniques of polynuclear aromatic hydrocarbon (PNA) compounds in six crude oil/bitumen samples provided by the Energy Research Laboratory (ERL) of the Canadian Institute of Mineral and Energy Technology (CANMET).

The samples were first processed by distillation to obtain the fractions boiling above 350°C. These distillation residues (b.p.>350°C) were then deasphaltened using n-pentane. The deasphaltened residues (maltene fractions) were further separated into compound types (saturates, mono-aromatics, diaromatics, polyaromatics, polar polyaromatics) by liquid-solid chromatography (LSC) using the API 60-CANMET/EMR developed procedure.

The compound-type separation was carried out in duplicate on each sample with excellent recoveries and good reproducibility being obtained. As expected, it was observed that increasing amounts of distillation residue in the samples yielded increasing amounts of the polyaromatics fraction and decreasing amounts of the saturates fraction. As the PNA compounds are contained in the polyaromatics fraction from each LSC separation, this fraction was the main subject for further study by instrumental analysis techniques.

Prior to instrumental analysis by high performance liquid chromatography (HPLC), gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS), each polyaromatics fraction was subjected to an acid/base extraction procedure to remove any polar material. Several of the sample fractions were analysed for carbon (C), hydrogen (H), nitrogen (N) and sulphur (S).

The "cleaned'up" polyaromatics fractions were fractionated by ring-size classes using normal-phase HPLC on polar stationary phases (diamine, amine and cyanoamine). A mixture of model PNA compounds was also subjected to this procedure and used to identify the ring-size classes. However, it was found that reversed-phase HPLC chromatograms of the polyaromatic fractions for both before and after the ring-size fractionation showed very similar profiles and indicated the presence of mainly 3-ring classes with a smaller amount of 4-ring classes. Additional fractionation studies were carried out on each polyaromatic fraction in order to remove high molecular weight coloured material. These studies involved molecular size separation by HPLC using a μ-Styragel (100Å) column in series with a μ-Spherogel (50Å) column. The PNA-enriched fraction was subjected to further analysis.

Methods for the analysis of a mixture of 24 PNA model compounds consisting of both methylated and unsubstituted PNA compounds were developed based on the chromatographic techniques of C_{18}-reversed-phase HPLC using ultraviolet and fluorescence detection (HPLC-UV/Fluorescence) and capillary GC using flame-ionization detection (GC-FID) and mass spectrometric characterization (GC-MS). These methodologies were subsequently used for the analysis and characterization of PNA compounds in the polyaromatic fractions.

The HPLC-UV/Fluorescence techniques were found to give limited information on the identification of compounds contained in the large number of well-resolved peaks observed in the chromatograms of all samples, because of the lack of suitable PNA model compounds.

The samples were quantitatively analyzed by capillary GC-FID with individual peaks tentatively identified by capillary GC-MS. The tentative identification showed that the PNA fraction in all samples consisted mostly of methylated derivatives of naphthalene, fluorene, anthracene, phenanthrene and pyrene, with methylated anthracene and phenanthrene compounds accounting for most of the PNA component of the distillation residue (b.p.>350°C) for each sample.

Studies using suitable model compounds, chemical-ionization mass spectrometry (CIMS) to differentiate between isomeric PNA compounds, and other structural methods such as NMR, are required for the absolute identification of PNA compounds in the distillation residues (b.p.>350°C).

Report ORF 82-5

CHEMICAL CHARACTERIZATION OF THE POLYNUCLEAR AROMATIC HYDROCARBONS IN FRACTIONS BOILING ABOVE 350°C

1. INTRODUCTION

This report on the above characterization study is submitted to DSS Consignee, the Department of Energy, Mines and Resources, CANMET, Energy Research Laboratories, Ottawa, Ontario. The work was carried out jointly by the United Technology & Science, Inc. (UTS) and the Ontario Research Foundation (ORF), with ORF acting as subcontractors for UTS. Sample preparation (Distillation and Deasphaltening) part of the work was carried out at UTS, and studies on the other aspects of the project were performed by ORF.

1.1 Objective

The objective of the work is the separation, characterization and instrumental analysis of polynuclear aromatic hydrocarbon (PNA) in six oil/bitumen samples provided by Energy, Mines and Resources (CANMET). Detailed compositional information on the PNA's in feedstocks, such as bitumens, heavy oils and their synthetic heavy products is necessary in order to help develop an effective utilization technology for such feedstocks. The objective as specified in the RFP is as follows: "Polynucelar aromatic hydrocarbons are the predominant aromatic type in bitumens, heavy oils and their synthetic heavy products. They have the potential to play a significant role in coke deposition in reactors during upgrading processes. Detailed study of the chemistry of PNA's present in processing products from increasing processing severities as well as at different levels in the reactor could give insight into the role of PNA's in the mechanism of coke formation."

1.2 Statement of Work

The work statement on the chemical characterization of the PNA's in six CANMET oil/bitumen samples is specified in the RFP and is as follows:

"1. Preparation of samples by distillation and deasphaltening to obtain the maltene fraction of the residues boiling above 350°C.

2. Hydrocarbon-type separation (saturates, monoaromatics, diaromatics, polyaromatics, and polar material) of these residues and using the polyaromatic concentrate for further investigation.

3. Using high performance liquid chromatagraphic (HPLC) sorbent-mobile phase system for separation of polynuclear aromatics according to fused aromatic ring number.

4. Chemical characterization of the separated polynuclear aromatic subclasses using instrumental analysis."

2. METHODOLOGY

Methods used in the present characterization study were partly based on the recommended procedures developed at CANMET. The six CANMET oil/bitumen samples were identified as follows:

(1) CANMET Sample #1 - solid
(2) CANMET Sample #2 - solid
(3) CANMET Sample #3 - solid
(4) CANMET Sample #4 - liquid (easily poured)
(5) CANMET Sample #5 - viscous liquid but pourable
(6) CANMET Sample #6 - liquid (easily poured)

The separation-characterization schematic diagram is shown in Figure 1.

2.1 Sample Preparation

2.1.1 Distillation

Six crude oil/bitumen samples were vacuum distilled in a spinning band still (having 1-4 litre/hour capacity and operated with Monel Band spinning at 2500 rpm - BFR Instrument Corporation, Pasadena, California, Model BFR 40T) with a still head temperature of 152°C and under a vacuum of 1 mm Hg. These conditions are equivalent to 350°C at atmospheric pressure. The fractions boiling above 350°C (152°C at 1 mm Hg) were used in this investigation.

CANMET Samples #1 and #2 when subjected to distillation showed no fraction boiling below 152°C at 1 mm Hg. With Samples #3 and #5, a small fraction of about 7% and 10% w/w respectively were collected in the distillate. The fractions boiling below 152°C at 1 mm Hg from Samples #4 and #6 were about 46% and 62% w/w respectively.

2.1.2 Deasphaltening

The distillation residue fraction (b.p.>350°C) from each sample was then subjected to deasphaltening using n-pentane. Asphaltenes were precipitated by adding about twenty volumes of pentane (glass distilled HPLC grade, Burdick-Jackson) to one volume of the distillation residue with occasional shaking for 24 hours at room temperature. The asphaltenes were first separated by filtration, and then extracted with pentane in a Soxhlet extractor until the solvent was colourless. The asphaltenes from the extractor were then air dried and the weight recorded. The Soxhlet pentane extract and the main pentane solubles were combined and the pentane removed under reduced pressure at 50°C to recover the maltene fraction. The weight of this fraction was then recorded. Table 1 summarizes the amount of crude oil/bitumen samples used, and the yield of maltene and asphaltene obtained in distillation and deasphaltening.

2.2 Hydrocarbon Type Separation by Liquid-Solid Chromatography

The deasphaltened distillation residues (maltenes) were separated into compound type concentrates of saturates, monoaromatics, diaromatics, polyaromatics and polar polyaromatics on a dual-packed silica gel-alumina liquid solid chromatographic system (LSC) developed by the USBM-API Project 60 and modified at the CANMET EMR Laboratory (1). The procedures used were as follows:

A stainless steel column, 10mm x 100cm was packed top-half with about 26 g activated silica (Davidson Grade 12, 28-200 mesh, activated at 250°C for 20 hours) and bottom half of the column packed with about 33 g activated alumina (ALCOA F-20, 38-200 mesh, activated at 400°C for 20 hours). The unfilled space at the top was filled with glass beads, and both ends of the column were plugged with glass wool.

A solution of the deasphaltened residue in pentane (1.0-1.5 g in 5 ml) was then placed at the top of the column and the solvents listed in Table 2 were used for the consecutive elution of the hydrocarbon types. A Milton Roy pumping system (LDC Mini Pump) was used to deliver solvents through the column.

The fractions of the column effluent were collected in test tubes and solvents evaporated using rotary evaporator under reduced pressure at 35°C, and Kuderna-Danish evaporative concentrator. After most of the solvents were evaporated, the fractions were transferred quantitatively to preweighed vials using appropriate solvents. The solvents were removed, and the vials were reweighed to determine the weight of the fraction. All CANMET samples were run in duplicate except Sample No. 5 which was run in triplicate. The polyaromatic fraction containing PNA from the above LSC was the main subject of this study.

2.3 Acid-Base Fractionation

The benzene eluates containing the polyaromatic fraction were subjected to "clean up" by acid-base extractions. The objective was to remove the polar organics from the polyaromatic fraction. The acid-base fractionation scheme used for "clean up" is shown in Fig. 2. After "clean up", the polyaromatic fraction concentrate was dissolved in 25 ml hexane containing 5% CH_2Cl_2. This solution was used for further separation by high performance liquid chromatography (HPLC) (both ring size and molecular size separation), and analysis by HPLC-UV/fluorescence and by gas chromatography (GC)-Flame ionization detection (FID) and GC-mass spectrometry (MS).

2.4 Elemental Analysis

Elemental analysis (C,H,N,S) of the crude samples, the maltenes and the asphaltenes and the polyaromatic fractions before and after acid-base fractionation were performed. In addition, the combined polar polyaromatic fraction (combined MeOH-Bz-ethyl ether, MeOH and pyridine eluates) of each sample was also analysed. Elemental analysis was performed by the Guelph Chemical Laboratory, Guelph, Ontario.

2.5 Reagents

All solvents used in the analysis were glass distilled HPLC grades (Burdick-Jackson). The following PNA compounds were used as reference standards: 3-methylphenanthrene (3-MePh), 2-methylanthracene (2-MeA), 9-MeA, 3,6-diMePh,

4-methylpyrene (4-MeP), 3-MeP, 1-MeP, 3,4-benzofluorene (3,4-BFl) (these PNA were received from the stock of CANMET EMR Laboratory); Ph, A, Fluorene (Fl), fluoranthene (F), pyrene (P), B{a}A, B{k}F, B{a}P, dibenz{ah}A, benz{ghi}perylene (received from the stock of the laboratory of Air Pollution Centre Directorate, Department of the Environment, Ottawa); and 2,3-BFl, triphenylene, 2,3-Benzph, 9,10-diMeB{a}A, perylene (Per), O-phenylenepyrene (Indeno 1,2,3-cd pyrene) (purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.).

2.6 Ring Size Separation by Normal Phase HPLC

The acid-base cleaned polyaromatic fractions of samples were studied for ring size fractionation using normal phase HPLC with three different polar stationary phases, namely diamine (Chromegabond diamine), amine (μ-Bondapak-NH_2) and cyanoamine (Partisil PAC). Mixtures of PNA model compounds were chromatographed under identical conditions to match the retention ranges of the peaks observed with the samples. The chromatographic conditions and the concentrations of the samples are shown in Tables 3 and 6A respectively.

2.7 Molecular Size Separation by SEHPLC

Both analytical and semipreparative SEHPLC (SE-size exclusion) were performed to further fractionate the acid-base cleaned polyaromatic fractions containing the high molecular weight and coloured materials. Two columns, μ-Styragel (100Å) in series with μ-Spherogel (50Å) were used with tetrahydrofuran (THF) at 1 ml/min as the mobile phase. The SEHPLC conditions are shown in Table 4, and the concentrations of samples used for analysis are shown in Table 6A. Mixtures of PNA model compounds were analysed under identical chromatographic conditions to match the elution volumes of the peaks observed with samples. Semipreparative SEHPLC was carried out with the following four samples: Sample #1-Expt. IX, Sample #3-Expt. XI, Sample #5-Expt. III and Sample #6-Expt. VII. In semipreparative work, multiple injections (50 or 250 μl) of the polyaromatic fraction dissolved in THF were made and four fractions from each sample were collected. The last fraction collected between 18-20 ml was light in colour and had elution volume similar to those observed with the mixture of 16 PNA standards. THF was removed from this fraction and the extract dissolved in hexane and analysed by GC-MS.

2.8 HPLC-UV and HPLC-Fluorescence Analysis

A mixture of 24 PNA standards, and the polyaromatic fractions of all samples were analysed by C_{18} reverse phase (RP) HPLC-UV and C_{18} RPHPLC-fluorescence detection technique using solvent program. The chromatographic conditions and the concentrations of the samples and standards used in the analysis are shown in Tables 5 and 6A respectively.

2.9 Capillary GC-FID and Capillary GC-MS Analysis

Capillary GC-FID and Capillary GC-MS techniques were used to analyse a mixture of 24 PNA standards and the polyaromatic fractions of all samples. The conditions used are shown in Table 6. A list of the PNA standards is given in Table 11, and the concentrations of the samples and the standards used for the analysis are found in Table 6A.

In addition, the polyaromatic fractions of four samples (Sample #1-Expt. IX, Sample #3-Expt. XI, Sample #5-Expt. III and Sample #6-Expt. VII) after being fractionated in semipreparative HPLC were analysed by GC-MS. Chromatographic conditions used were similar to those in Table 6, except that a 2 µl injection volume and a mixture of 17 PNA as reference standards were used.

3. RESULTS & DISCUSSION

3.1 Distillation & Deasphaltening

A summary of the distillation and the deasphaltening results is shown in Table 7. The results suggest that the samples with larger amount of distillation residue (b.p. >350°C) have the lower maltene/asphaltene ratio. For example, the Sample #6 with 38% distillation residue content gave a ratio of 47, whereas Sample #1 and Sample #2 - both samples with almost 100% residue had a ratio of around 3.8.

3.2 Hydrocarbon Type Separation, Acid-Base Fractionation of Polyaromatic Concentrate and Elemental Analysis

The deasphaltened distillation residue (maltenes) of the six samples were separated into hydrocarbon type concentrates by API 60 method modified by CANMET [1]. The LSC system showed good separation (see LSC chromatograms of the samples in Figures 3-8) and good reproducibility in duplicate experiments. Table 8 summarizes the results of % hydrocarbon recoveries

obtained in LSC separation of the deasphaltened distillation residues of the samples, and Table 8A shows the variation of the hydrocarbon types with the yields of the distillation residues. The data in Table 8A suggests that an increase in the yield of residue results in an increase in polyaromatic as well as in polar polyaromatic content, and at the same time shows a decrease in saturates content in the deasphaltened distillation residue.

The benzene eluate containing the polyaromatic concentrate from the LSC system was subjected to "clean up" by acid-base fractionation following procedures shown in Figure 2. The objective was to remove the polar organics from the polyaromatic fraction. The recoveries from acid-base extraction "clean up" were high with all six samples (see Table 9). The "cleaned up" polyaromatic fraction was taken for further study.

The results of the elemental analysis (C,H,N,S) of the polyaromatic concentrate before and after acid-base "clean up" are shown in Table 10. Since no NMR studies were performed, evaluation of aromatic and aliphatic carbon content in the polyaromatic fractions of the samples was not possible. The crude samples and their respective maltene and asphaltene fractions, and the polar polyaromatic fractions (combined eluates - 60% MeOH:20% benzene: 20% ethyl ether, methanol and pyridine) from the LSC of each maltene sample were also analysed for C,H,N,S (see Table 10).

3.3 HPLC Separation

3.3.1 Ring Size Fractionation

The polyaromatic concentrates of all samples were analysed by normal phase HPLC using Chromegabond diamine polar stationary phase according to procedures developed at EMR, CANMET[2]. Chmielowiec and George[3] have shown that diamine bonded phases yield a sequence in PNA separation based on condensed ring number, regardless of alkyl substitution. The objective in the present study was to use the prefractionation technique on the diamine bonded phases for the separation of PNA compounds in the polyaromatic concentrate according to ring classes, e.g. 3-ring (phenanthrene/anthracene

group), 4-ring (pyrene group) and >4-ring classes (B{a}P, etc.), prior to the final analysis by GC-FID, GC-MS and other instrumental techniques.

Figures 9 and 10 show the chromatographic profiles of the samples in normal phase HPLC using Chromegabond diamine as the stationary phase. The chromatograms of a mixture of 16 PNA consisting of 3-ring, 4-ring and >4-ring PNA (see Table 3) are shown in both figures. All samples showed identical chromatograms with one large peak matching with the retention time range of 3-ring class PNA. In addition, all samples showed two small shoulder peaks which correspond to the retention time of 4-ring PNA. This was more prominent with the Samples #4, 5 and 6 (samples containing low distillation residue and polyaromatic content) than the other three samples with high polyaromatic and distillation residue content.

The separations achieved on the Chromegabond diamine column were studied in more detail with one sample. The polyaromatic fraction of Sample #5 (Expt. I) was subjected to semipreparative HPLC fractionation using the same conditions as in Table 3, but with a semipreparative UV cell and 250 µl injection. A 5 ml solution (2.8 mg/ml) was fractionated with multiple injection (20 x 250 µl) and two fractions - one corresponding to Peak I and the other fraction corresponding to Peaks II and III (see Fig. 10, Sample #5) were collected and analysed by C_{18}RPHPLC under isocratic conditions. A HPLC chromatogram of Fraction I (the major 3-ring class PNA fraction) in Figure 10A shows the presence of a large number of well-resolved peaks in this fraction. However, the Fraction II also gave similar chromatographic profiles probably due to cross-contamination in the semipreparative fractionation work. Various attempts for improved resolution by optimization of flow rate, sample concentration, injection volume, etc., were unsuccessful. Subsequent studies have shown that the non-fractionated polyaromatic starting material when analysed by C_{18}RPHPLC under identical conditions also gave a chromatographic profile which is similar to those obtained with the above two cut fractions suggesting that the ring size prefractionation on Chromegabond diamine may not be necessary prior to final analysis of the types of samples under study dominated mainly by one single class of 3-ring PNA compounds.

Other polar stationary phases such as amine (μ-Bondapak-NH_2), cyanoamine (Partisil PAC) for the separation of PNA into ring classes by normal phase HPLC have been reported[4,5]. The polyaromatic concentrates of all CANMET samples were analysed on such columns (see Figures 11 and 12 for chromatograms in μ-Bondapak-NH_2 and Figures 13 and 14 for chromatograms in Partisil PAC). The chromatographic profiles were found similar to those observed on Chromegabond diamine, showing a main large peak with retention time ranges of mainly 3-ring class PNA compounds.

3.3.2 Molecular Size Fractionation

The polyaromatic fractions of all samples were highly colored, and the intensity of the color increased greatly with samples having high distillation residue and polyaromatic content. The colored materials originating possibly from the high molecular weight and highly condensed polyaromatics cause interferences in GC-FID/GC-MS analysis. A study was therefore made to "clean up" the polyaromatic fraction from such colored and high molecular weight materials by size exclusion HPLC (SEHPLC) using μ-Styragel (100 Å, exclusion limit 10^3 MW {molecular wight}) in series with μ-Spherogel (50 Å, exclusion limit 5×10^2 MW). SEHPLC profiles of the six samples and a mixture of 10 PNA standards are shown in Figure 15. (The samples are polyaromatic concentrates from duplicate LSC experiments). All PNA in the standard mixture (MW ranging between 166-276) were eluted at an elution volume of between 18-20 ml (THF at 1 ml/min, see conditions in Table 4 and 5A), which was very close to the permeation volume of the columns.

All samples showed a peak at elution volume of between 18-20 ml similar to that observed with PNA standards. However, all samples except Sample #4 (the least colored fraction) contained varying amounts of high molecular weight materials which are excluded first from the column in SEHPLC. Samples #5 and 6 seem to contain lower amounts of high molecular weight compound than the three samples (#1, #2 and #3). The polyaromatic fractions with the most intense color from the three crude solid samples (#1, #2 and #3) having high distillation residue and polyaromatic content showed in addition to a shoulder peak at elution volume of 18-20 ml, a large peak at elution volume of between 10-12 ml which corresponds to the presence of compounds

having MW much higher than 276 in such fractions (similar high molecular weight compound peaks were also observed in Sample #5 and #6 but at low intensity). The above observations suggest that the major component in the polyaromatic fractions of the three samples (#1, #2 and #3) are largely high molecular weight materials.

The molecular size separationsachieved on the μ-Styragel + μ-Spherogel columns were studied in more detail with four samples (Sample #1, #3, #5 and #6 - duplicate experiments). In order to facilitate subsequent characterization study by GC-MS, the polyaromatic concentrates of the above four samples were fractionated by semipreparative SEHPLC under conditions used in the analytical study, and the PNA containing fraction at elution volumes of between 18-20 ml was collected and analysed by GC-MS. The collected fractions were slightly colored, indicating that most of the high molecular weight colored materials have been removed in the SEHPLC fractionation process.

3.4 HPLC-Fluorescence and HPLC-UV Analysis

Six polyaromatic fractions and a mixture of 24 PNA model compounds have been analysed by C_{18}RPHPLC-fluorescence detection technique. The analysis gave very little information on the characterization of PNA compounds in the samples. This is due to the fact that both alkylated and parent 3-ring class and <3-ring class PNA compounds show poor senstivity in fluorescence. This is substantiated in the HPLC chromatograms of the 24 PNA standards, which showed the peaks of only 8 PNA compounds with 4-ring and >4-ring structures. The chromatogram of the PNA standards and the retention times are shown in Figure 16 and Table 11 respectively. The chromatograms of the six samples run under identical solvent program and other conditions as the standard mixture are shown in Figures 17-22. A large number of fluorescent peaks eluting at and after fluoranthene were observed. Some of these peaks have been tentatively characterized by comparing the relative retention times (relative to fluoranthene) with those of the PNA standards. This is shown in Table 11A.

The samples and a mixture of 24 PNA standards were also analysed by C_{18}RPLC-UV (254 nm) under chromatographic conditions similar to those used in the above HPLC-fluorescence analysis. An excellent separation of the PNA compounds was achieved using solvent programs, and the chromatogram and the retention data are shown in Figure 23 and Table 11 respectively. Chromatograms of the six samples run under identical program and other conditions as the standard mixture are shown in Figures 24-29. All samples showed well-resolved peaks, but due to the lack of standard reference PNA, characterization of all the peaks are not possible. Only some of the major peaks observed in the sample have been tentatively characterized by comparing the relative retention times (relative to anthracene) with those of the PNA standards. This is shown in Table 11B.

3.5 Capillary GC-FID and Capillary GC-MS Analysis

The high complexity of the PNA mixture in the polyaromatic fractions as is evidenced from their HPLC-UV chromatogram needs the greatest resolution possible in their analysis. In this respect, GC with glass or recently fused silica capillary columns gives the best resolution of PNA currently available. The high separation efficiency of fused silica capillary column combined with the identification power of MS were used in the present study for the analysis of the polyaromatic concentrates of all samples.

A variety of stationary phases has been employed in capillary column separation of PNA compounds, but because of their moderate selectivities and high temperature stabilities, SE-52 (methylsilicone gum with 5% phenyl groups) and SE-54 (methylsilicone gum with 1% vinyl and 5% phenyl groups) have gained wide acceptance. In the present GC-FID analytical study, an SE-54 fused silica capillary column was used. The same SE-54 column was then used as part of a Hewlett-Packard Model 5992B combined gas chromatography/mass spectrometer/data system to obtain mass spectral information on resolved components in the complex polyaromatic fraction.

Initially, chromatographic resolution of a mixture of the same 24 PNA model compounds that was used in HPLC-Fluor/UV studies was examined by both GC-FID and GC-MS techniques, run under identical chromatographic conditions. Excellent resolution of the PNA reference compounds was obtained in both systems as shown in Figures 30 (GC-FID) and 37 (GC-MS). The retention times, and the relative retention times (relative to 2-Me Anthracene) from both systems, showed very little difference. Retention data are shown in Table 11. The table also contains the retention indices of the 24 PNA model compounds calculated using the equation shown in the footnote of the table using naphthalene, phenanthrene, triphenylene and picene as standards. The retention indices obtained with GC-FID analysis of model compounds on SE-54 column are found in good agreement with those reported in the literature[6]. The retention indices are useful in identifying unknown PNA peaks when such PNA reference compounds are not available.

Mass spectra of the individual twenty-four PNA compounds are shown in Appendix I and some useful mass spectral data in Table 11. The electron impact mass spectra of PNA generated in the present study are distinctive, mainly consisting of an intense molecular ion $(M)^+$ and lower intensity ions, $(M-1)^+$, etc., due to loss of one to four hydrogen atoms. The $(M+1)^+$ ion is always present and is due mainly to the ^{13}C isotope. Doubly charged molecular ions are quite common and are usually near 20% of the abundance of the molecular ion $(M)^+$. Alkylated PNA demonstrate the normal $(M-15)^+$, $(M-29)^+$, etc., fragmentation pattern for alkyl chains even in the case of methyl substituted compounds. The $(M-15)^+$ ion is lower in abundance for methyl substituted compounds than it is for PNA with longer alkyl side chains. In the case of alkylated PNA, the $(M)^+$ ion may not dominate the spectra, but is nevertheless strong and easily recognized.

Capillary GC-MS chromatograms of the polyaromatic fractions of the six CANMET samples are shown in Figures 38 through 43. The PNA compounds identified by GC-MS and some of their spectral data are given in Tables 12 through 17, respectively, and the corresponding mass spectra are given

in Appendix II through VII respectively. In the above study, the structural assignments of a large number of PNA and their isomers present in all samples were made by analysing the mass spectra, and by making comparisons with the retention data of PNA reference standards, and whenever possible, by comparison of the acquired spectra with those of the reference PNA compounds.

GC-FID chromatograms of the polyaromatic fractions of the six samples that were simultaneously obtained under identical chromatographic conditions as used in GC-MS are compared in Figures 31 through 36. The major GC-FID peaks were then assigned proper PNA structures by the comparison of the retention data (both retention time and retention time relative to 2-MeA) with those of PNA compounds identified in GC-MS study. The PNA in each sample were quantitated based on the response of 2-MeA, using a peak area method for calibration and calculation. The concentration data are shown in Tables 12 through 17. These data are semiquantitative. PNA standards were not available for many of the PNA components identified, and therefore response factors were not applied to the data in the tables.

Capillary GC-MS chromatograms of the PNA enriched fractions isolated from the polyaromatic concentrates of the four samples by SEHPLC fractionation (see Section 3.3.2) are shown in Figures 45 through 48. (A GC-MS chromatogram of a mixture of 17 PNA standards run under the identical conditions is shown in Figure 44 with mass spectral data given in Appendix 1A.) The PNA compounds identified in these samples are given in Tables 18 through 21 respectively, and the corresponding mass spectra of the PNA identified are given in Appendix IIA, IVA, VIA and VIIA. This study indicates that a very similar PNA type of compound identified in the non-fractionated samples are also present in the SEHPLC fractionated samples. The SEHPLC fractionated polyaromatic concentrates used in the GC-MS work were from duplicate LSC experiments.

A summary of the PNA identified in the samples and arranged according to PNA classes of compounds are given in Table 22. The characterization study has shown that the PNA fraction in all CANMET samples consists

mostly of methylated derivatives of naphthalene (2-ring), fluorene (3-ring), anthracene (3-ring), phenanthrene (3-ring) and pyrene (4-ring), and their isomers with methylated anthracene and phenanthrene compounds accounting for most of the PNA component of the distillation residue (b.p.>350°C) for each sample.

The positive identification of most of the isomeric PNA components in the complex mixture of the distillation residue is presently impossible because of lack of standard reference compounds. Comparison of chromatographic retention data and mass spectral information about mixture constituents with data from synthesized reference compounds is necessary. In most cases, differentiation of PNA isomers by electron impact mass spectra used in the present study cannot be achieved. The use of chemical ionization mass spectrometry (CIMS) and other structural methods, such as NMR, are needed to unequivocally assign structures.

D.M. Kane, Ph.D.
Senior Scientist
United Technology and Science, Inc.

B.S. Das, Ph.D.
Research Scientist
Ontario Research Foundation

BSD:gmb

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TABLES

(Tables 1 - 22)

Table 1: Quantities of Crude Samples used and Yield of Maltenes and Asphaltenes in Distillation and Deasphaltening

CANMET Sample No.	Initial Weight used in Distillation (g)	Weight of Distillation Residue, b.p.>350°C (g)	Transferred for Deasphaltening (g)	Sample Loss in Transference (g)	Volume of Pentane used (ml)	Weight of Asphaltene (g)	Weight of Maltene (g)
1	48.2	47.3	all	0.92	800-900	9.75	36.63
2	59.1	58.6	50.4	0.50	800-900	10.31	39.59
3	82.2	76.3	60.5	0.18	1200-1300	13.83	46.49
4	104.0	56.2	all	4.50	900-1000	13.03	44.8
5	98.6	88.2	all	9.16	2000	2.24	70.87
6	108.0	41.4	all	0.92	800-900	0.86	39.62

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Table 2: Eluents and Order of Elution used in LSC Compound Type Fractionation of Maltenes

Eluent	Compound Type
Pentane	Saturates
5% Benzene in Pentane	Monoaromatics
15% Benzene in Pentane	Diaromatics
Benzene	Polyaromatics
Methanol:Benzene:Ethyl Ether (60:20:20)	Polar Polyaromatics
Methanol	
Pyridine	
Benzene	

Table 3: HPLC Conditions in Ring Size Fractionation of Acid-Base Cleaned Polyaromatic Fractions of CANMET Samples

HPLC Parameters	Chromegabond Diamine	μBondapak-NH_2	Partisil PXS 10/25 PAC
Instrument	Spectra-Physics Model 3500	Spectra Physics Model 3500	Spectra Physics Model 3500
Column Manufacturer	4.6mm x 30cm, 10 μm ES Industries	3.9mm x 30cm, 10 μm Waters Associates	4.6mm x 25cm, 10 μm Whatman
Mobile Phase	96% Hexane:4% CH_2Cl_2	95% Hexane:5% CH_2Cl_2	Hexane
Flow Rate	1.20 ml/min	1.20 ml/min	1.20 ml/min
Injection Volume	10μℓ	10μℓ	10μℓ
Detector	Schoffel Model SF770 UV @ λ254nm	Beckman Model 153 UV @ λ254nm	Beckman Model 153 UV @ λ254nm
Temperature	Ambient	Ambient	Ambient
PNA Standards	Fluorene(Fl), Phenanthrene(Ph), Anthracene(A), 3-Me Ph, 2-Me A, 9-Me A, Fluoranthene, Pyrene(P), 3-Me P, 4-Me P, 1-Me P, B(a)A, B(a)P, B(k)F, Dibenz(ah)A, Benz(ghi)Per	Fluorene, Phenanthrene(Ph), Anthracene(A), Fluoranthene, Pyrene, B(a)A, B(k)F, B(a)P, Dibenz(ah)A, Benz(ghi)Per	Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, B(a)A

Table 4: HPLC Conditions in Molecular Size Fractionation of Acid-base Cleaned Polyaromatic Fractions of CANMET Samples

Instrument	Beckman Model 112
Columns	μStyragel (100Å, 7.8mm x 30cm Waters Associates) in series with μSpherogel (50Å, 8.0mm x 30cm, Beckman)
Mobile Phase	Tetrahydrofuran
Flow Rate	1.00 ml/min
Injection Volume	50μℓ
Detector	Beckman Model 153 UV @ 254nm
Temperature	Ambient
PNA Standards	Fluorene, Phenanthrene(Ph), Anthracene, Fluoranthene, Pyrene, B{a}A, B{k}F, B{a}P, Dibenz{ah}A, Benz{ }P

Table 5: HPLC/UV and HPLC/Fluorescence Conditions for Analysis of Acid-Base Cleaned Polyaromatic Fractions of CANMET Samples

HPLC Parameter	
Instrument	Beckman HPLC Model 322
Column	C_{18} RP Ultrasphere ODS, 5µm (4.6mm x 25cm) Beckman
Mobile Phase	Solvent A - 50% CH_3CN Solvent B - 100% CH_3CN
Solvent Program	50% CH_3CN to 100% CH_3CN in 50 min, hold at 100% CH_3CN for 15 min, 100% CH_3CN to 50% CH_3CN in 15 min.
Flow Rate	1.0 ml/min
Injection Volume	50µℓ
Detector	Fluorescence-Schoeffel Model 970 λex 280nm, λem 389nm, Sensitivity 4.40 Attenuation 0.5µA, Time Constant 5 sec. UV - Vari-Chrom. @ 254nm
Temperature	Ambient
PNA Standards	Fl, Ph, A, F, 3-MePh, 9-MeA, Py, 3,4-BenzoFl, 2-MeA, Triphenylene, 2,3-BenzoFl, 3,6-DiMePh, B{a}A, 2,3-BenzoPh, 1-MeP, 3-MeP, 4-MeP, Per, B{k}F, 9,10-DiMeB{a}A, B{a}P, Dibenz{ah}A, O-phenylenePyrene, Benz{ghi}Per

Table 6: Capillary GC-FID & Capillary GC-MS Conditions for Analysis of Polyaromatic Fractions of CANMET Samples

GC-FID Conditions	
Instrument	Varian 3700
Column	15m x 0.2mm SE-54 fused silica capillary
Flow Rate	2 ml/min N_2
Injector Temp.	270°C
Injection Mode	Splitless to vent 30 sec.
Program Conditions	5°/min; Initial Temp:70°C; Final Temp:275°C
Detector	FID (H_2 flow:30ml/min; air flow:300ml/min)
Detector Temp.	300°C
Injection Volume	3µl
Data Processor	SP 4000 (Spectra-Physics)
PNA Standards	See Table 11
GC-MS Conditions	
Instrument	Hewlett-Packard 5992B
Column	15m x 0.2mm SE-54 fused silica capillary
Flow Rate	2ml/min He
Injector Temp.	270°C
Program Conditions	5°/min; Initial Temp:70°C; Final Temp:275°C
Injection Volume	5µl
PNA Standards	See Table 11
MS Conditions	Electron Impact
Multiplier Voltage	2400 e.m.v.
MS Peak Detect Threshold	10 Linear Counts
Samples per 0.1 AMU	4
Scan Speed	380 amu/sec
Scan range	30-300 mass units

Sample No.	Expt. No.	Initial Conc. in 5% CH_2Cl_2 in Hexane	SEHPLC Fractionation μstyragel & μspherogel	Ring Size Fractionation			HPLC/Fluor in MeOH	HPLC/UV in MeOH	GC/FID in Hexane	GC/MS in Hexane
				Chromegabond Diamine	μBondapak NH_2	Partisil PAC				
1	X	226mg/25ml (9mg/ml)	-	1:10	1:10	1:10	1:25	None	5:1	5:1
1	IX	171mg/25ml (6.84mg/ml)	1:5	-	-	-	-	-	-	-
2	XIII	231mg/25ml (9.25mg/ml)	-	1:5	1:5	1:5	1:10	10:1	10:1	10:1
2	XIV	188mg/25ml (7.52mg/ml)	1:10	-	-	-	-	-	-	-
3	XII	200mg/25ml (8.0mg/ml)	-	1:5	1:5	1:5	1:10	10:1	10:1	10:1
3	XI	190mg/25ml (7.6mg/ml)	1:10	-	-	-	-	-	-	-
4	IV	138mg/25ml (5.5mg/ml)	-	1:10	1:10	1:10	1:100	1:10	None	None
4	V	115mg/25ml (4.6mg/ml)	1:10	-	-	-	-	-	-	-
5	I	74mg/25ml (2.9mg/ml)	-	1:5	1:5	1:5	1:20	None	5:1	5:1
5	III	158mg/25ml (6.32mg/ml)	1:5	-	-	-	-	-	-	-
6	VI	68mg/25ml (2.7mg/ml)	-	1:5	1:5	1:5	1:40	1:1	None	None
6	VII	60mg/25ml (2.4mg/ml)	1:1	-	-	-	-	-	-	-
24 PNA Standards		see Table 11	-	-	-	-	1:500	None	None	None
16 PNA Standards		see Tables 11 & 3	-	1:1	-	-	-	-	-	-
10 PNA Standards		see Tables 11 & 3	-	-	1:1	-	-	-	-	-
6 PNA Standards		see Tables 11 & 3	-	-	-	1:1	-	-	-	-
10 PAN Standards		see Tables 11 & 4	1:1	-	-	-	-	-	-	-

Table 7: Summary of Distillation and Deasphaltening Results

CANMET Sample #	Fraction Boiling Above 350°C, % w/w	Maltenes % w/w		Asphaltenes % w/w		Maltene/ Asphaltene Ratio
		of crude oil/bitumen	of residues b.p.>350°C	of crude oil/bitumen	of residues b.p.>350°C	
1	98.1	77.5	79.0	20.6	21.0	3.8
2	99.2	78.7	79.3	20.5	20.7	3.8
3	92.8	71.5	77.1	21.3	22.9	3.4
4	54.0	51.4	95.2	2.6	4.8	19.8
5	89.7	75.7	84.4	14.0	15.6	5.4
6	38.3	37.5	97.9	0.8	2.1	46.9

Table 8: Compound Type Distribution in CANMENT Sample Deasphaltened Residues >350°C (Wt%)

Eluents*	CANMET Sample No. 6		CANMET Sample No. 5			CANMET Sample No. 4		CANMET Sample No. 3		CANMET Sample No. 2		CANMET Sample No. 1	
	Expt. VI (1.1137 g)	Expt. VII (1.0147 g)	Expt. I (1.3261 g)	Expt. II (1.3057 g)	Expt. III (1.2584 g)	Expt. IV (1.3389 g)	Expt. V (1.0587 g)	Expt. XI (1.0221 g)	Expt. XII (1.0325 g)	Expt. XIII (1.3092 g)	Expt. XIV (1.1479 g)	Expt. IX (1.0295 g)	Expt. X (1.3544 g)
Pentane	55.55	55.91	19.30	21.64	17.06	37.54	38.67	17.02	17.62	18.22	18.87	19.99	18.00
5% Benzene in Pentane	13.55	15.44	11.08	12.92	8.48	7.45	12.98	12.65	14.45	11.21	12.27	10.79	10.41
15% Benzene in Pentane	8.69	8.06	9.52	11.47	8.64	25.97	16.04	13.51	7.30	13.76	15.55	10.92	10.74
Benzene	6.10 (0.0679 g)	8.31 (0.0843 g)	12.60 (0.1671 g)	12.31 (0.1607 g)	13.56 (0.1707 g)	10.37 (0.1389 g)	10.54 (0.1116 g)	18.85 (0.1927 g)	19.30 (0.1993 g)	20.75 (0.2716 g)	22.27 (0.1785 g)	16.92 (0.1742 g)	18.10 (0.2452 g)
MeOH-Benzene-Et. Ether	1.21	1.01	2.97	2.52	2.72	1.77	2.40	2.51	2.83	2.14	14.18	2.92	2.25
Methanol	11.38	9.43	27.74	25.66	24.51	16.30	13.10	30.34	28.61	22.19	5.42	27.06	26.57
Pyridine	1.55	3.64	3.08	3.45	2.97	0.86	2.37	3.90	4.27	3.77	5.28	3.04	4.86
Benzene	0.11	0.05	0.15	0.47	0.62	0.34	0.05	0.45	0.46	0.20	0.13	0.31	0.31
Total	98.63	101.85	86.43	90.44	78.56	100.60	96.15	99.23	94.84	92.24	93.97	91.95	91.24

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*See Table 2.

Table 8A: Variation of Hydrocarbon Types with Yield of Distillation Residue

Sample	Yield of Dist. Residue Fraction >350°C Wt%	Hydrocarbon Types in Deasphaltened Residue >350°C (Wt %)			
		Average Polyaromatic Content	Average Polar Polyaromatic Content	Average Combined Mono & Diaromatic Content	Average Saturates Content
No. 6	38.3	7.2	14.36	22.86	55.73
No. 4	54.0	10.45	18.4	31.22	38.10
No. 5	89.7	12.45	31.87	20.70	20.47
No. 3	92.8	19.07	36.23	23.95	17.32
No. 1	98.1	17.51	33.35	21.43	18.99
No. 2	99.2	21.51	26.49	26.39	18.54

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Table 9: % Recovery of the Polyaromatics in Acid-Base Extraction

	CANMET Sample No. 6		CANMET Sample No. 5		CANMET Sample No. 4		CANMET Sample No. 3		CANMET Sample No. 2		CANMET Sample No. 1	
	Expt. VI	Expt. VII	Expt. I*	Expt. III	Expt. IV	Expt. V	Expt. XI	Expt. XII	Expt. XIII	Expt. XIV	Expt. X	Expt. IX
Amount used in cleanup (mg)	67.9	84.3	139.35	170.70	138.90	111.60	192.70	199.30	260.74	178.50	245.20	167.23
Amount recovered (mg)	68.9	60.6	73.78	158.40	138.40	115.30	190.10	206.80	231.80	188.20	225.90	171.50
% Recovery	101.47%	71.89%	52.95%	92.79%	99.64%	103.32%	98.65%	103.76%	88.90%	105.43%	92.13%	102.55%

* This sample was subjected to both acid base and solvent partitioning cleanup with nitromethane

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Table 10: Elemental Analysis (Wt. %) of CANMET Oil/Bitumen Samples

Sample Identification	% C	% H	% N	% S
Sample 1				
Crude oil/bitumen	82.77	10.95	0.13	6.16
Asphaltene	78.57	8.79	0.70	8.44
Maltene	83.56	10.87	0.00	5.34
Polyaromatic fraction (before Acid/Base fractionation)	81.78	9.3C	0.00	9.06
Polyaromatic fraction (after Acid/Base fractionation)	81.59	9.51	0.00	6.43
Combined polar polyaromatic fraction*	77.55	9.82	0.87	7.26
Sample 2				
Crude oil/bitumen	82.97	10.90	0.16	5.95
Asphaltene	78.61	8.76	0.62	8.24
Maltene	83.36	11.29	0.00	5.56
Polyaromatic fraction (before Acid/Base fractionation)	81.26	9.00	0.00	9.73
Polyaromatic fraction (after Acid/Base fractionation)	80.76	8.98	0.00	10.43
Combined polar polyaromatic fraction*	77.14	9.93	0.96	6.71
Sample 3				
Crude oil/bitumen	82.80	10.95	0.36	5.93
Asphaltene	80.84	7.97	1.47	6.24
Maltene	83.39	11.29	0.00	5.34
Polyaromatic fraction (before Acid/Base fractionation)	78.67	9.44	0.00	8.14
Polyaromatic fraction (after Acid/Base fractionation)	76.58	9.95	0.00	8.13
Combined polar polyaromatic fraction*	73.94	9.64	0.97	7.12

Table 10: Elemental Analysis (Wt. %) of CANMET Oil/Bitumen Samples

...cont'd

Sample Identification	% C	% H	% N	% S
Sample 4				
Crude oil/bitumen	83.04	12.75	0.38	3.84
Asphaltene	65.19	4.83	1.63	3.51
Maltene	86.03	10.60	0.00	3.48
Polyaromatic fraction (before Acid/Base fractionation)	87.22	7.00	0.00	5.49
Polyaromatic fraction (after Acid/Base fractionation)	87.73	6.56	0.00	5.68
Combined polar polyaromatic fraction*	85.40	7.51	3.25	3.87
Sample 5				
Crude oil/bitumen	82.49	10.76	1.73	5.59
Asphaltene	74.85	8.39	0.96	8.23
Maltene	83.22	11.08	0.00	5.66
Polyaromatic fraction (before Acid/Base fractionation)	80.86	8.85	0.00	8.42
Polyaromatic fraction (after Acid/Base fractionation)	80.89	9.65	0.00	6.69
Combined polar polyaromatic fraction*	80.84	9.67	0.91	6.73
Sample 6				
Crude oil/bitumen	83.20	14.55	0.78	1.59
Asphaltene	70.80	8.13	0.52	4.56
Maltene	85.07	12.77	0.00	2.00
Polyaromatic fraction (before Acid/Base fractionation)	85.29	9.25	0.00	5.35
Polyaromatic fraction (after Acid/Base fractionation)	84.55	9.05	0.00	6.02
Combined polar polyaromatic fraction*	82.92	11.05	0.99	4.30

*Combined eluates (60% MeOH:20% Benzene:20% Et. Ether, Methanol & Pyridine) from LSC.

Table 11: Capillary GC and HPLC Data of PNA Model Compounds

PNA Standard	Peak No.***	Mol. Wt.	Conc. µg/ml	Capillary GC-MS Chromatogram in Fig. 37 Mass Spectrum in Appendix I				Capillary GC-FID Chromatogram in Fig. 30				HPLC/UV Chromatogr. in Fig. 23	HPLC/Fluor. Chromatogr. in Fig. 16
				Ret. Time (min)	Rel. Ret. Time*	Base peak M+	Spectrum No.	Ret. Time (min)	Rel. Ret. Time*	Calc. Ret. Index†	Lit. Ret. Index§	Ret. Time (min)	Ret. Time (min)
Fluorene (Fl)	33	166	7.70	13.32	0.660	166	2	13.28	0.654	267.90	268.17	27.26	**
Phenanthrene (Ph)	12	178	4.00	17.56	0.870	178	4	17.55	0.864	300.00	300.00	29.17	**
Anthracene (A)	12A	178	0.14	17.76	0.880	178	5	17.75	0.874	301.52	301.69	30.49	**
3-Me Ph	13	192	1.12	19.94	0.988	192	6	20.01	0.985	319.55	319.46	34.03	**
2-Me A	13A	192	1.10	20.18	1.000	192	7	20.31	1.000	322.11	321.57	36.16	**
9-Me A	34	192	1.70	21.12	1.046	192	8	21.26	1.046	329.61	329.13	34.31	**
3,6-Di Me Ph	35	206	1.50	22.18	1.099	206	10	22.28	1.096	337.83	337.83	38.67	**
Fluoranthene (F)	21	202	9.00	23.12	1.145	202	12	23.15	1.140	344.77	344.01	33.35	31.03
Pyrene (P)	21A	202	11.64	24.06	1.192	202	13	24.06	1.185	352.19	351.22	34.89	**
4-Me P	22C	216	3.60	26.26	1.301	216	15	26.38	1.299	370.71	369.54	41.02	**
3,4-Benzo Fl (Benzo[c] Fl	36	216	9.60	26.26	1.301	216	15A	26.38	1.299	370.71	-	36.16	**
2,3-Benzo Fl (Benzo[b] Fl	37	216	5.25	26.26	1.301	216	15B	26.38	1.299	370.71	369.39	37.40	**
3-Me P	22D	216	4.80	26.76	1.326	216	16	26.91	1.324	375.34	-	40.03	**
1-Me P	22D-1	216	4.50	26.76	1.326	216	16	26.91	1.324	375.34	373.55	40.03	**
B[a]A	26	228	7.70	29.76	1.474	228	18	29.91	1.472	398.88	398.50	39.21	37.09
Triphenylene	38	228	5.00	29.88	1.480	228	19	30.06	1.480	400.00	400.00	37.40	**
2,3-benzo ph	39	228	6.60	29.88	1.480	228	19	30.06	1.480	400.00	-	39.21	**
B[k]F	40	252	9.60	34.44	1.706	252	24	34.83	1.714	441.29	442.56	44.43	42.58
9,10-Di Me B[a]A	41	256	24.80	34.62	1.715	256	25	35.00	1.723	442.50	-	45.70	43.87
B[a]P	29	252	8.10	35.56	1.762	252	26	35.95	1.770	450.77	453.44	45.70	44.18
Perylene (Per)	42	252	6.80	35.88	1.777	252	27	36.30	1.787	453.71	456.22	43.94	**
O-phenylene P	43	276	8.80	39.62	1.963	276	31	40.18	1.987	487.41	481.87	50.13	48.62
Dibenz[ah]A	44	278	15.20	39.94	1.979	278	32	40.50	1.994	489.91	495.45	47.78	46.16
Benz[ghi]Per	45	276	8.20					41.03	2.02	496.0	501.32	50.53	49.00

* Relative to the retention time of 2-Me A

† Retention indices were calculated from the equation: $I = 100 \frac{T_R(\text{substance}) - T_R(C_z)}{T_R(C_{z+1}) - T_R(C_z)} + 100\,Z$, where $T_R(C_z)$ and $T_R(C_{z+1})$ are defined as the retention times for the PAH internal standards which bracket the substance of interest with retention time, T_R and Z is the number of rings in the PAH standard that elute prior to the substance of interest. Naphthalene, phenanthrene, triphenylene and picene were used as internal standards.

§ See Lee et al. Anal. Chem. 51, 768 (1979).

** No response at the concentration used.

*** Numbers refer to peaks in GC chromatograms.

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Table 11A: Tentative Identification of PNA in Samples by Retention Time in HPLC-Fluorescence Analysis

Sample #1 Chromatogram (Fig. 17)			Sample #2 Chromatogram (Fig. 18)			Sample #3 Chromatogram (Fig. 19)			Sample #4 Chromatogram (Fig. 20)			Sample #5 Chromatogram (Fig. 21)			Sample #6 Chromatogram (Fig. 22)		
Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified	Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified	Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified	Ret. Time of Major Peaks	Rel. Ret. Time**	PNA** Identified	Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified	Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified
31.31	1.00	1	31.36	1.00	1	31.01	1.00	1	30.73	1.00	1	30.91	1.00	1	31.03	1.00	1
36.58	1.168		36.63	1.168		31.83	1.026		31.47	1.024		36.12	1.168		31.80	1.025	
37.19	1.188	2	37.39	1.192	2	36.30	1.171		32.29	1.051		36.77	1.189	2	36.32	1.170	
41.17	1.135		41.16	1.312		36.91	1.190	2	34.19	1.112		37.49	1.212		36.90	1.189	2
41.78	1.334		41.80	1.333		37.66	1.214		34.56	1.125		40.68	1.316		37.69	1.215	
42.64	1.362	3	42.83	1.366	3	40.83	1.317		35.99	1.171		41.31	1.336		41.11	1.325	
44.04	1.406	4	44.10	1.406	4	41.41	1.335		36.82	1.198	2	42.33	1.369	3	41.50	1.337	
45.02	1.438		45.84	1.462		42.26	1.362	3	38.20	1.243		44.07	1.426	5	44.45	1.432	
46.18	1.475		46.22	1.473		43.76	1.411	4	38.80	1.262		45.80	1.482	7	45.69	1.472	
46.85	1.496		46.86	1.494		44.18	1.424	5	39.59	1.288		46.46	1.503		46.69	1.504	
47.68	1.522		47.72	1.522		46.56	1.501		40.49	1.317		48.18	1.559		48.41	1.560	6
48.52	1.549		48.51	1.547		47.31	1.525		43.72	1.422	5	48.71	1.576	8	49.40	1.592	
50.74	1.620		49.80	1.588		48.31	1.558		44.48	1.447					50.56	1.629	
			50.69	1.616		50.42	1.626		46.16	1.502							
									48.77	1.587							

*Retention time relative to Fluoranthene.

**Relative retention time of the PNA standards calc. from Table II HPLC-Fluor Data are as follows:
1-(F)-1.00, 2-(B(a)A) 1.195, 3-(B(k)F) 1.372, 4-(9,10 DIMeB(a)A) 1.414
5-(B(a)P) 1.424, 6-(Indeno (1,2,3cd)P) 1.567, 7-(Dibenz(ah)A) 1.487
and 8-(Benz(ghi)Per) 1.579

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Table 118: Tentative Identification of PNA in Samples by Retention Time in HPLC-UV Analysis

Sample #1 Chromatogram (Fig. 24)			Sample #2 Chromatogram (Fig. 25)			Sample #3 Chromatogram (Fig. 26)			Sample #4 Chromatogram (Fig. 27)			Sample #5 Chromatogram (Fig. 28)			Sample #6 Chromatogram (Fig. 29)		
Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified	Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified	Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified	Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified	Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified	Ret. Time of Major Peaks	Rel. Ret. Time*	PNA** Identified
						26.06	0.877										
28.19	0.953	2	28.09	0.952	2	28.32	0.953	2	28.66	0.953	2	28.40	0.954	2	28.49	0.956	2
29.58	1.00	3	29.48	1.00	3	29.71	1.00	3	30.06	1.00	3	29.76	1.0	3	29.80	1.00	3
33.31	1.126	6	31.10	1.055		31.30	1.054		31.71	1.054		31.95	1.073		30.50	1.023	
34.05	1.151	6A	33.16	1.125	6	32.13	1.081	4	32.30	1.074		33.45	1.124	6	31.63	1.061	
36.34	1.229	8	33.92	1.151	6A	33.42	1.125	6	33.04	1.099	4	34.15	1.147	6A	32.33	1.085	4
37.68	1.274	9	35.34	1.199		34.13	1.149	6A	33.76	1.123	6	35.53	1.194		33.69	1.131	6
38.33	1.296		36.19	1.228	8	35.63	1.199		34.53	1.148	6A	36.03	1.211	8	34.38	1.153	
39.16	1.326	11	36.65	1.243		36.08	1.214		35.96	1.196		36.82	1.237		35.86	1.203	
39.85	1.347	12	37.55	1.274	9	36.50	1.228	8	36.45	1.212		37.74	1.268	9	36.23	1.216	
40.57	1.371		38.23	1.297		37.82	1.273	9	36.80	1.224	8	38.41	1.291		36.57	1.227	8
41.22	1.393		39.03	1.324	11	38.52	1.296		37.28	1.240		39.16	1.315	11	37.27	1.251	
41.75	1.411		39.73	1.348	12	39.34	1.324	11	38.47	1.279	10	39.86	1.339	12	37.98	1.274	9
42.49	1.436	13	40.43	1.371		40.06	1.348	12	38.84	1.292		40.59	1.364		38.66	1.297	
42.93	1.451	14	41.14	1.395		40.74	1.371		39.63	1.318	11	41.24	1.385		39.41	1.322	
43.78	1.480		41.58	1.410		41.50	1.397		40.37	1.342	12	41.68	1.400		40.10	1.346	12
44.70	1.511		42.35	1.437	13	41.44	1.412		41.01	1.364		42.44	1.426		40.59	1.362	
45.21	1.528		42.76	1.450	14	42.62	1.434	13	41.73	1.388		42.80	1.438	13	41.26	1.384	
47.27	1.598		43.70	1.482		43.10	1.451	14	42.19	1.403		43.12	1.448		41.95	1.408	
48.19	1.629		45.06	1.528		43.95	1.479		42.73	1.421		43.65	1.467		42.70	1.433	
49.59	1.673		45.52	1.544		44.03	1.482		43.33	1.441	13	43.84	1.473		43.06	1.444	13
50.14	1.695		45.73	1.551		45.37	1.527		43.75	1.465	14	45.03	1.513		43.92	1.474	
50.43	1.705		46.12	1.564	16	45.86	1.543		44.19	1.470		45.47	1.527		44.82	1.504	
50.62	1.711		46.45	1.576		46.45	1.563	16	44.54	1.481		46.07	1.548		45.30	1.520	
			49.23	1.669		46.78	1.574		45.13	1.501	15	46.34	1.557	16	45.79	1.536	
			49.48	1.678		47.12	1.586					46.74	1.571		46.32	1.554	
			50.05	1.697		48.41	1.629					48.00	1.612		47.01	1.577	16
			50.62	1.717		49.83	1.677					49.89	1.676		49.57	1.663	18
						50.36	1.695										

*Retention time relative to Anthracene.

**Relative retention time of the PNA standards calc. from Table 11 HPLC-UV data are as follows:

2-(Ph) 0.956, 3-(A) 1.000, 4-(F) 1.093, 6-(9-MeA) 1.125, 6A (P) 1.144, 8-(triphenylene/2,3BFl) 1.226, 9-(3,6 DiMePh) 1.268, 10-(2,3 BFl/B(a)A) 1.285, 11-(1MeP/3MeP) 1.312, 12-(4MeP) 1.345, 13-(Per) 1.441, 14-(B(k)F) 1.457, 15-(9,10 DiMeB(a)A/B(a)P) 1.498, 16-(Dibenz(ah)A) 1.644 & 18-(Benz(ghi)Per) 1.657

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Table 12: PNA Compositional Analysis of CANMET Sample #1 (Acid-Base Cleaned Polyaromatic Fraction, Expt. X)

PNA Compound [a,b]	Peak[e] No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 38 Mass Spectrum in Appendix II				Capillary GC - FID Analysis Chromatogram in Figure 31				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time[c]	PNA Content in[d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350°C (µg/g)[d]	PNA Content in crude oil/bitumen (µg/g)[d]
Anthracene	12A	178	17.82	M^+	35	Same spectrum as standard.					
Penta Me Naph	8	198	19.38	M^+	39	$(M-15)^+$ peak absent.					
Penta Me Naph	8B	198	19.82	M^+	42	Very weak $(M-15)^+$ peak.					
3 Me Ph	13	192	20.32	M^+	44	$(M-15)^+$ peak absent. Complex spectrum (mixture).					
2 Me A	13A	192	20.39	M^+	45	$(M-15)^+$ peak absent. Same spectrum as standard.	20.05	1.000	1.2467	0.1782	0.1748
Me Ph/Me A	13B	192	20.82	M^+	46	$(M-15)^+$ peak absent. Spectrum similar to No. 45.					
Me Ph/Me A	13C	192	20.88	M^+	47	$(M-15)^+$ peak absent. Spectrum similar to No. 45.					
Trimethylfluorene	3B	208	21.12	$(M-15)^+$	48	Strong M^+ peak at 208.	21.20	1.0341	0.3148	0.0451	0.0442
Hexa Me Naph	9A	212	21.50	M^+	50	Medium strong $(M-15)^+$ peak.	21.66	1.0566	0.4213	0.0602	0.0591
Hexa Me Naph	9B	212	21.94	M^+	52	Medium strong $(M-15)^+$ peak.					
Hexa Me Naph	9C	212	22.32	M^+	53	Medium strong $(M-15)^+$ peak.	22.41	1.0932	0.7606	0.1088	0.1067
Di Me Ph/Di Me A	14B	206	22.76	M^+	54	Strong $(M-15)^+$ peak. Complex spectrum (mixture).	22.81	1.1127	1.2300	0.1785	0.1751
Di Me Ph/Di Me A	14D	206	23.12	M^+	55	Strong $(M-15)^+$ peak.	23.05	1.1244	0.9592	0.1371	0.1345
Di Me Ph/Di Me A	14E	206	23.26	M^+	56	Strong $(M-15)^+$ peak.	23.23	1.1332	1.1754	0.1680	0.1648
Di Me Ph/Di Me A	14F	206	23.32	M^+	57	Strong $(M-15)^+$ peak.					
Di Me Ph/Di Me A	14G	206	23.50	M^+	58	Strong $(M-15)^+$ peak. Complex spectrum (mixture).	23.51	1.1469	0.7349	0.1051	0.1031

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Table 12: PNA Compositional Analysis of CANMET Sample #1
(Acid-Base Cleaned Polyaromatic Fraction, Expt. X)

...cont'd

PNA Compound [a,b]	Peak No.[c]	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 38 Mass Spectrum in Appendix II				Capillary GC - FID Analysis Chromatogram in Figure 31				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time[c]	PNA Content in[d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350°C (g/g)[d]	PNA Content in crude oil/bitumen (µg/g)[d]
Hepta Me Naph	10	226	23.76	M^+	59	Strong $(M-15)^+$ peak. Complex mixture with Di Me Ph A.					
Di Me Ph/Di Me A	14H	206	24.00	M^+	61	Strong $(M-15)^+$ peak. Complex spectrum (mixture).	24.15	1.1780	1.0020	0.1433	0.1406
Hepta Me Naph	10A	226	24.38	M^+	63	Strong $(M-15)^+$ peak.	24.46	1.1931	3.7720	0.5393	0.5291
Hepta Me Naph	10B	226	24.62	M^+	64	Strong $(M-15)^+$ peak.	24.76	1.2078	3.3585	0.4802	0.4711
Hepta Me Naph	10C	226	24.94	M^+	67	Strong $(M-15)^+$ peak.					
Hepta Me Naph	10D	226	25.00	M^+	68	Strong $(M-15)^+$ peak.					
Tri Me Ph/Tri Me A	15A	220	25.26	M^+	69	Strong $(M-15)^+$ peak.					
Tri Me Ph/Tri Me A	15B	220	25.38	M^+	70	Strong $(M-15)^+$ peak.	25.18	1.2283	5.2757	0.7543	0.7400
Tri Me Ph/Tri Me A	15C	220	25.68	M^+	71	Strong $(M-15)^+$ peak.	25.46	1.2419	2.2035	0.3151	0.3091
Tri Me Ph/Tri Me A	15D	220	25.82	M^+	72	Strong $(M-15)^+$ peak. Complex spectrum (mixture).	25.61	1.2493	1.0253	0.1466	0.1438
Tri Me Ph/Tri Me A	15E	220	26.12	M^+	74	Strong $(M-15)^+$ peak.					
Tri Me Ph/Tri Me A	15F	220	26.50		76	Strong $(M-15)^+$ peak. Complex mixture with Octa Me Naph.	26.10	1.2732	1.7104	0.2445	0.2399
Tri Me Ph/Tri Me A	15G	220	26.82		77	Strong $(M-15)^+$ peak.	26.65	1.3000	11.4106	1.6317	1.6007
Octa Me Naph	11B	240	26.94	M^+	78	Strong $(M-15)^+$ peak. Complex mixture with tetra Me Ph A.	26.93	1.3137	0.1967	0.1553	0.1524
Me Py/BFl	22E	216	27.06	M^+	79	$(M-15)^+$ peak absent. Same as standard.	27.18	1.3259	0.5432	0.0777	0.0762
Octa Me Naph	11C	240	27.32	M^+	80	Strong $(M-15)^+$ peak.	27.41	1.3371	1.6843	0.2409	0.2363

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Table 12: PNA Compositional Analysis of CANMET Sample #1
(Acid-Base Cleaned Polyaromatic Fraction, Expt. X)

...cont'd

PNA Compound [a,b]	Peak[e] No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 38 Mass Spectrum in Appendix II				Capillary GC - FID Analysis Chromatogram in Figure 31				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time[c]	PNA Content in[d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350°C (µg/g)[d]	PNA Content in crude oil/bitumen (µg/g)[d]
Tetra Me Ph/Tetra Me A	16A	234	27.50	M^+	81	Strong $(M-15)^+$ peak. Complex mixture with Octa Me Naph.					
DiMecyclopentenoPh	32A	232	27.82	$(M-15)^+$	82	M^+ peak at 232.	27.75	1.3536	1.5220	0.2176	0.2135
Tetra Me Ph/Tetra Me A	16B	234	27.94	M^+	83	Strong $(M-15)^+$ peak.					
Tetra Me Ph/Tetra Me A	16C	234	28.26	M^+	84	Strong $(M-15)^+$ peak. Complex spectrum (mixture).	28.21	1.3761	0.9123	0.1304	0.1279
Pentamethylfluorene	5	236	28.32	M^+	85	Strong $(M-15)^+$ peak.	28.36	1.3834	1.1333	0.1620	0.1589
Tetra Me Ph/Tetra Me A	16E	234	29.06	M^+	88	$(M-15)^+$ peak absent. Mixture with DI Me P F	29.01	1.4151	3.5697	0.5104	0.5007
DI Me Py	23D	230	29.50	M^+	90	$(M-15)^+$ peak present. Complex spectrum (mixture)	29.51	1.4395	2.2728	0.3250	0.3188
Penta Me Ph/Penta Me A	17A	248	30.76	M^+	94	Very weak $(M-15)^+$ peak.	30.83	1.5039	2.6867	0.3842	0.3769
Penta Me Ph/Penta Me A	17C	248	31.50	M^+	96	$(M-15)^+$ peak absent.					
Hepta Me Ph/Hepta Me A	19	276	34.76	M^+	106	Medium strong $(M-15)^+$ peak.					
Hepta Me Ph/Hepta Me A	19A	276	35.12	M^+	107	Strong $(M-15)^+$ peak.					
Octa Me Ph/Octa Me A	20	290	35.94	M^+	108	Complex					
Octa Me Ph/Octa Me A	20A	290	36.38	M^+	109	Complex					
									51.12	7.43	7.29

[a] Tentative identification.

[b] See footnotes in Table 22.

[c] Relative to the retention time of 2-Me A

[d] Based on the response of 2-Me A

[e] Numbers refer to peaks in GC chromatograms.

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Table 13: PNA Compositional Analysis of CANMET Sample #2
(Acid-Base Cleaned Polyaromatic Fraction, Expt. XIII)

PNA Compound [a,b]	Peak No.[c]	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 39 Mass Spectrum in Appendix III				Capillary GC - FID Analysis Chromatogram in Figure 32				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time[c]	PNA Content in Polyaromatic Fr. (µg/g)[d]	PNA Content in Distillation Residue b.p. >350°C (µg/g)[d]	PNA Content in crude oil/bitumen (µg/g)[d]
Di Me Ph/Di Me A	14G	206	23.56	M^+	65	Strong $(M-15)^+$ peak	24.20	1.1915	0.7380	0.1215	0.1205
Hepta Me Naph	10B	226	24.62	M^+	68	Strong $(M-15)^+$ peak	24.53	1.2078	0.3483	0.0573	0.0569
Tri Me Ph/Tri Me A	15A	220	25.32	M^+	70	Strong $(M-15)^+$ peak	25.23	1.2422	1.0775	0.0177	0.0176
Tri Me Ph/Tri Me A	15B	220	25.62	M^+	71	Strong $(M-15)^+$ peak	25.73	1.2669	1.3157	0.2166	0.2149
Tri Me Ph/Tri Me A	15C	220	26.68	M^+	74	Strong $(M-15)^+$ peak	26.37	1.2984	2.7564	0.4537	0.4501
Octa Me Naph	11C	240	27.44	M^+	76	Strong $(M-15)^+$ peak Complex spectrum (mixture)	27.48	1.3530	0.3161	0.0520	0.0516
Tetra Me Ph/Tetra Me A	16B	234	27.94	M^+	77	Strong $(M-15)^+$ peak	28.10	1.3836	0.6367	0.1049	0.1041
Tetra Me Ph/Tetra Me A	16E	234	29.12	M^+	81	$(M-15)^+$ peak absent. Complex spectrum (mixture)	29.18	1.4367	1.6858	0.2775	0.2753
Penta Me Ph/Penta Me A	17A	248	30.82	M^+	84	Very weak $(M-15)^+$ peak. Complex spectrum (mixture)	30.92	1.5224	0.5339	0.0879	0.0872
Hexa Me Ph/Hexa Me A	18	262	32.62	M^+	87	Weak $(M-15)^+$ peak					
Hexa Me Ph/Hexa Me A	18A	262	33.00	M^+	89	$(M-15)^+$ peak absent					
Hepta Me Ph/Hepta Me A	19	276	34.82	M^+	97	Medium strong $(M-15)^+$ peak					
Hepta Me Ph/Hepta Me A	19A	276	35.18	M^+	98	Medium strong $(M-15)^+$ peak					
									9.30	1.3891	1.3782

a,b,c,d & e See footnotes in Table 12.

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Table 14: PNA Compositional Analysis of CANMET Sample #3
(Acid-Base Cleaned Polyaromatic Fraction, Expt. XII)

PNA Compound [a,b]	Peak No.[e]	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 40 Mass Spectrum in Appendix IV				Capillary GC - FID Analysis Chromatogram in Figure 33				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time[c]	PNA Content in[d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350°C (µg/g)[d]	PNA Content in crude oil/bitumen (µg/g)[d]
Methylfluorene	1A	180	16.12	$(M-15)^+$	258	Strong M^+ peak at 180.	15.95	0.7896	0.3010	0.0447	0.0415
Phenanthrene	12	178	17.68	M^+	262	Spectrum similar to standard	17.45	0.8639	1.5514	0.2307	0.2141
Dimethylfluorene	2	194	18.18	$(M-29)^+$	263	Strong $(M-15)^+$ and M^+ peaks. Ethyl fl. or mixture with Di Me fl.					
Dimethylfluorene	2A	194	18.50	$(M-15)^+$	264	Strong M^+ peak at 194.	18.31	0.9064	0.4962	0.0741	0.0688
Dimethylfluorene	2B	194	18.68	$(M-15)^+$	265	Strong M^+ peak at 194.	18.51	0.9163	1.6774	0.2493	0.2314
Dimethylfluorene	2C	194	18.88	$(M-15)^+$	266	Strong M^+ peak at 194.	18.63	0.9222	2.8279	0.4205	0.3902
Dimethylfluorene	2D	194	19.44	$(M-15)^+$	268	Strong M^+ peak at 194.	19.25	0.9529	0.5369	0.0798	0.0741
Penta Me Naph	8A	198	19.68	M^+	269	$(M-15)^+$ peak absent.	19.46	0.9634	0.4907	0.0729	0.0677
Penta Me Naph	8B	198	20.00	M^+	271	$(M-15)^+$ peak absent.	19.86	0.9832	1.2303	0.1829	0.1697
3 Me Ph	13	192	20.26	M^+	272	$(M-15)^+$ peak absent. Spectrum similar to standard.	20.05	0.9962	6.5203	0.9695	0.8997
2 Me A	13A	192	20.38	M^+	273	$(M-15)^+$ peak absent. Spectrum similar to standard.	20.20	1.0000	0.5549	0.0825	0.0766
Me Ph/Me A	13B	192	20.62	M^+	274	$(M-15)^+$ peak absent. Spectrum similar to standard.	20.45	1.0124	5.4229	0.8063	0.7483
Trimethylfluorene	3	208	20.68	$(M-29)^+$	275	Strong M^+ and $(M-15)^+$ peaks. Mixture with Di Me fl.	20.53	1.0163	10.5449	1.5680	1.4551
Trimethylfluorene	3A	208	21.00	$(M-15)^+$	276	Strong M^+ peak at 208.	20.81	1.0301	0.2820	0.0365	0.0389
Trimethylfluorene	3B	208	21.12	$(M-15)^+$	277	Strong M^+ peak at 208.	20.93	1.0361	1.0120	0.1504	0.1396
Hexa Me Naph	9	212	21.32	M^+	278	$(M-15)^+$ peak at 197.	21.11	1.0450	0.3447	0.0512	0.0475

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Table 14: PNA Compositional Analysis of CANMET Sample #3 (Acid-Base Cleaned Polyaromatic Fraction, Expt. XII)

...cont'd

PNA Compound [a,b]	Peak No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 40 Mass Spectrum in Appendix IV				Capillary GC - FID Analysis Chromatogram in Figure 33				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time[c]	PNA Content in Polyaromatic Fr. (µg/g)[d]	PNA Content in Distillation Residue b.p. >350°C (µg/g)[d]	PNA Content in crude oil/bitumen (µg/g)[d]
Trimethylfluorene	3C	208	21.56	M^+	280	Strong $(M-15)^+$ at 193.	21.46	1.0624	1.0893	0.1620	0.1503
Hexa Me Naph	9A	212	21.76	M^+	281	Med. strong $(M-15)^+$ peak.	21.58	1.0683	2.9593	0.4401	0.4084
Trimethylfluorene	3D	208	21.94	$(M-15)^+$	282	Strong M^+ peak at 208 Mixture	21.83	1.0807	1.0717	0.1594	0.1479
Hexa Me Naph	9B	212	22.12	M^+	283	Med. strong $(M-15)^+$ peak.	21.96)	1.0871)	5.7170	0.8501	0.7899
Hexa Me Naph	9C	212	22.44	M^+	284	Strong $(M-15)^+$ peak.	22.03)	1.0906)			
Di Me Ph/Di Me A	14A	206	22.62	M^+	285	$(M-15)^+$ peak at 191.	22.31	1.1044	11.1911	1.6909	1.5692
Hexa Me Naph	9D	212	22.76	M^+	286	Weak $(M-15)^+$ peak. Complex spectrum (mixture).					
Di Me Ph/Di Me A	14B	206	22.88	M^+	287	Strong $(M-15)^+$ peak.	22.78	1.1277	13.2348	1.9680	1.8263
Di Me Ph/Di Me A	14C	206	23.00	M^+	288	Strong $(M-15)^+$ peak.	22.91	1.1341	4.0838	0.6073	0.5636
Di Me Ph/Di Me A	14D	206	23.12	M^+	289	Strong $(M-15)^+$ peak.	23.00	1.1386	6.6412	0.9876	0.9165
Di Me Ph/Di Me A	14F	206	23.32	M^+	290	Strong $(M-15)^+$ peak.	23.18	1.1475	5.2729	0.7840	0.7276
Di Me Ph/Di Me A	14G	206	23.50	M^+	291	Strong $(M-15)^+$ peak. Mixture with tetra Me Fl.	23.43	1.1599	1.9353	0.2893	0.2685
Di Me Ph/Di Me A	14H	206	23.82	M^+	292	Strong $(M-15)^+$ peak.	23.70	1.1732	1.6272	0.2420	0.2246
Tetramethylfluorene	4A	222	24.06	$(M-15)^+$	293	Strong M^+ peak at 222.					
Di Me Ph/Di Me A	14I	206	24.18	M^+	294	Strong $(M-15)^+$ peak.	24.09	1.1911	1.6282	0.2420	0.2246
Hepta Me Naph	10A	226	24.38	M^+	295	Strong $(M-15)^+$ peak.	24.31	1.2034	9.7521	1.4502	1.3458
Hepta Me Naph	10B	226	24.76	M^+	297	Strong $(M-15)^+$ peak.	24.65	1.2203	10.6407	1.5823	1.4684
Hepta Me Naph	10C	226	24.88	M^+	298	Strong $(M-15)^+$ peak.					

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Table 14: PNA Compositional Analysis of CANMET Sample #3 (Acid-Base Cleaned Polyaromatic Fraction, Expt. XII)

...cont'd

PNA Compound [a,b]	Peak [e] No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 40 Mass Spectrum in Appendix IV				Capillary GC - FID Analysis Chromatogram in Figure 33				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time [c]	PNA Content in [d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350°C (µg/g) [d]	PNA Content in crude oil/bitumen (µg/g) [d]
Tri Me Ph/Tri Me A	15	220	25.00	M^+	299	Strong $(M-15)^+$ peak					
Tri Me Ph/Tri Me A	15A	220	25.12	M^+	300	Strong $(M-15)^+$ peak (Mixture)	24.91	1.2331	2.9242	0.4348	0.4035
Tri Me Ph/Tri Me A	15B	220	25.44	M^+	301	Strong $(M-15)^+$ peak (Mixture)	25.08	1.2416	12.0211	1.7876	1.6589
Tri Me Ph/Tri Me A	15C	220	25.82	M^+	302	Strong $(M-15)^+$ peak (Mixture)					
Tri Me Ph/Tri Me A	15D	220	25.88	M^+	303	Strong $(M-15)^+$ peak (Mixture)					
Octa Me Naph	11	240	26.00	$(M-15)^+$	304	Strong M^+ peak at 240. Complex spectrum (mixture)					
Tri Me Ph/Tri Me A	15E	220	26.26	M^+	305	Strong $(M-15)^+$ peak Complex spectrum (mixture)					
Tri Me Ph/Tri Me A	15F	220	26.50	M^+	306	Strong $(M-15)^+$ peak	26.46	1.3099	10.5198	1.5643	1.4517
Octa Me Naph	11A	240	26.68	M^+	307	Strong $(M-15)^+$ peak Complex spectrum (mixture)					
Me Py/BF	22D	216	26.76	M^+	308	$(M-15)^+$ peak absent Very complex spectrum	26.78	1.3257	5.0652	0.7532	0.6990
Octa Me Naph	11C	240	27.26	M^+	312	Strong $(M-15)^+$ peak	27.00) 27.11)	1.3366) 1.3421)	4.4059	0.6551	0.6079
Di Me CPPh	32	232	27.56	$(M-15)^+$	314	M^+ peak at 232 Mixture with Octa Me Naph	27.26	1.3495	2.6789	0.3983	0.3696
Tetra Me Ph/Tetra Me A	16A	234	27.68	M^+	315	Strong $(M-15)^+$ peak	27.36	1.3544	1.6147	1.0776	0.2228
Tetra Me Ph/Tetra Me A	16B	234	28.00	M^+	316	Very complex spectrum	27.60) 27.78)	1.3663) 1.3752)	7.6603	1.1391	1.0571

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Table 14: PNA Compositional Analysis of CANMET Sample #3
(Acid-Base Cleaned Polyaromatic Fraction, Expt. XII)

PNA Compound [a,b]	Peak[e] No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 40 Mass Spectrum in Appendix IV				Capillary GC - FID Analysis Chromatogram in Figure 33				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time[c]	PNA Content in[d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350°C (µg/g)[d]	PNA Content in crude oil/bitumen (µg/g)[d]
Tetra Me Ph/Tetra Me A	16D	234	28.76	M^+	320	$(M-15)^+$ peak absent	28.85	1.4282	3.1109	0.4626	0.4293
Tetra Me Ph/Tetra Me A	16E	234	29.18	M^+	321	Very weak $(M-15)^+$ peak Complex	29.33	1.4519	3.1570	0.4694	0.4356
Hexamethylfluorene	6	250	29.62	M^+	322	$(M-15)^+$ peak present Complex spectrum	29.63	1.4669	1.6558	0.2462	0.2285
Hexamethylfluorene	6A	250	30.06	M^+	323	$(M-15)^+$ peak med. strong	30.21	1.4955	1.4175	0.2108	0.1956
Penta Me Ph/Penta Me A	17	248	30.44	M^+	324	$(M-15)^+$ peak absent	31.46	1.5574	3.6453	0.5420	0.5030
									170.5147	26.2155	23.5563

a,b,c,d & e See footnotes in Table 12.

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Table 15: PNA Compositional Analysis of CANMET Sample #4
(Acid-Base Cleaned Polyaromatic Fraction, Expt. IV)

PNA Compound [a,b]	Peak No.[e]	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 41 Mass Spectrum in Appendix V				Capillary GC - FID Analysis Chromatogram in Figure 34				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time[c]	PNA Content in[d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350°C (µg/g)[d]	PNA Content in crude oil/bitumen (µg/g)[d]
Methylfluorene	1	180	16.00	$(M-15)^+$	101	Strong M^+ peak at 180	15.97	0.7898	2.5313	0.2498	0.1349
Methylfluorene	1A	180	16.12	$(M-15)^+$	102	Strong M^+ peak at 180					
Tetra Me Naph	7	184	17.06	M^+	103	$(M-15)^+$ peak absent					
Phenanthrene	12	178	17.68	M^+	106	Spectrum similar to standard	17.47	0.8640	84.2959	8.3207	4.4932
Anthracene	12A	178	17.88	M^+	107	Spectrum similar to standard	17.68	0.8744	16.2937	1.6083	0.8685
Dimethylfluorene	2A	194	18.50	$(M-15)^+$	109	Strong M^+ peak at 194					
Dimethylfluorene	2B	194	18.68	$(M-15)^+$	110	Strong M^+ peak at 194	18.63	0.9214	52.6199	5.1941	2.9048
Dimethylfluorene	2C	194	18.82	$(M-15)^+$	111	Strong M^+ peak at 194					
Dimethylfluorene	2D	194	19.38	$(M-15)^+$	113	Strong M^+ peak at 194					
Penta Me Naph	8A	198	19.68	M^+	114	$(M-15)^+$ peak absent					
3 Me Ph	13	192	20.26	M^+	116	Spectrum similar to standard	20.05	0.9916	119.6731	11.8128	6.3789
2 Me A	13A	192	20.38	M^+	117	Spectrum similar to standard	20.22	1.0000	22.9229	2.2628	1.2219
Me Ph/Me A	13B	192	20.68	M^+	118	$(M-15)^+$ peak absent Mixture with Tri Me Fl	20.50	1.0138	54.7257	5.4018	2.9170
Trimethylfluorene	3A	208	21.06	$(M-15)^+$	120	Strong M^+ peak at 208					
Cyclopenteno Ph (CPPh)	3C	204	21.68	M^+	122		21.55	1.0658	36.7278	3.6254	1.9577
Trimethylfluorene	3D	208	21.94	M^+	123	$(M-15)^+$ peak at 193 Complex spectrum (mixture)					
Di Me Ph/Di Me A	14	206	22.38	M^+	125	Strong $(M-15)^+$ peak at 191 Mixture with Hexa Me Naph					
Di Me Ph/Di Me A	14A	206	22.50	M^+	126	Strong $(M-15)^+$ peak. Spectrum similar to standard	22.43	1.1093	50.4298	4.9780	2.6881

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Table 15: PNA Compositional Analysis of CANMET Sample #4
(Acid-Base Cleaned Polyaromatic Fraction, Expt. IV)

...cont'd

PNA Compound [a,b]	Peak [c] No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 41 Mass Spectrum in Appendix V				Capillary GC - FID Analysis Chromatogram in Figure 34				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time [c]	PNA Content in [d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350°C (µg/g) [d]	PNA Content in crude oil/bitumen (µg/g) [d]
Di Me Ph/Di Me A	14B	206	22.56	M^+	127	Strong $(M-15)^+$ peak Spectrum similar to standard					
Di Me Ph/Di Me A	14C	206	23.06	M^+	131	$(M-15)^+$ peak present (Mixture)	22.93	1.1340	35.4679	3.5009	1.8905
Fluoranthene	21	202	23.26	M^+	132	Spectrum similar to standard	23.10	1.1424	65.1339	6.4294	3.4719
Trimethylfluorene	3E	208	23.82	M^+	134	$(M-15)^+$ absent (Mixture)	23.72	1.1731	54.2814	5.3580	2.8933
Pyrene	21A	202	24.26	M^+	135	Spectrum similar to standard	24.08	1.1909	232.7423	22.9739	12.4059
Hepta Me Naph	10A	226	24.38	204	136	Mixture with CPPh (M^+ 204)	24.25	1.1993	61.6602	6.0343	3.2585
Hepta Me Naph	10B	226	24.68	M^+	137	Strong $(M-15)^+$ peak	24.63	1.2181	23.6192	2.3314	1.2599
Tri Me Ph/Tri Me A	15	220	25.06	M^+	138	Med. $(M-15)^+$ peak Mixture with Di Me Py	24.97	1.2349	22.3592	2.2070	1.1918
MeCPPh	31	218	25.18	M^+	139	Strong $(M-15)^+$ peak Complex					
Me P/BFl	22	216	25.50	M^+	140	Spectrum similar to standards	25.38	1.2552	42.7207	4.2169	2.2771
Tri Me Ph/Tri Me A	15B	220	25.62	M^+	141	$(M-15)^+$ peak absent					
Me P/BFl	22A	216	25.82	M^+	142	Spectrum similar to standards Slightly complex					
Me P/BFl	22B	216	26.00	M^+	143	Mixture with Di CPPh	25.98	1.2849	56.9690	5.6226	3.0362
4-Me P/BFl	22C	216	26.44	M^+	144	Spectrum similar to standards	26.35	1.3031	176.9308	17.4646	9.4309
Me CPPh	31A	218	26.56	M^+	145	Strong $(M-15)^+$ peak	26.52	1.3116	93.4867	9.2242	4.9811
Me CPPh	31B	218	26.76	M^+	146	Weak $(M-15)^+$ peak	26.73	1.3219	89.6710	8.8513	4.7797

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Table 15: PNA Compositional Analysis of CANMET Sample #4
(Acid-Base Cleaned Polyaromatic Fraction, Expt. IV)

...cont'd

PNA Compound [a,b]	Peak[e] No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 41 Mass Spectrum in Appendix V				Capillary GC - FID Analysis Chromatogram in Figure 34				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time[c]	PNA Content In[d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350°C (µg/g)[d]	PNA Content in crude oil/bitumen (µg/g)[d]
Di Me CPPh	32	232	27.50	$(M-15)^+$	149	M^+ peak at 232 Complex spectrum (Mixture)	27.53	1.3615	18.1598	1.7924	0.9679
Tetra Me Ph/Tetra Me A	16A	234	27.76	M^+	150	Complex Spectrum (Mixture)					
Tetra Me Ph/Tetra Me A	16B	234	27.82	M^+	151	Complex Spectrum (Mixture)					
Di Me P	23	230	28.12	M^+	152	Strong $(M-15)^+$ peak	28.08	1.3887	49.0439	4.8409	2.6141
Di Me P	23A	230	28.38	M^+	153	Weak $(M-15)^+$ peak	28.43	1.4060	62.3679	6.1563	3.3244
Tetra Me Ph/Tetra Me A	16D	234	28.76	M^+	154	$(M-15)^+$ peak absent	28.75	1.4218	106.9251	10.5544	5.6994
Tetra Me Ph/Tetra Me A	16E	234	29.06	M^+	155	$(M-15)^+$ peak absent					
Di Me CPPh	32B	232	29.18	M^+	156	Complex Spectrum					
Di Me CPPh	32C	232	29.50	M^+	157	Complex Spectrum	29.65	1.4664	26.2412	2.5902	1.3987
B[a]A	26	228	29.82	M^+	158	Spectrum Similar to Standard					
Tri Me P	24	244	30.00	M^+	159	Strong $(M-15)^+$ at 229 Mixture with B[a]A	30.13	1.4901	56.0633	5.5339	2.9883
Penta Me Ph/Penta Me A	17	248	30.38	M^+	161	$(M-15)^+$ peak absent	30.50	1.5084	45.4204	4.4833	2.4210
Penta Me Ph/Penta Me A	17A	248	30.76	M^+	162	$(M-15)^+$ peak absent	30.88	1.5272	51.2635	5.0602	2.7325
Penta Me Ph/Penta Me A	17B	248	31.18	M^+	163	$(M-15)^+$ peak absent Complex spectrum					
Me B[a]A	27	242	32.26	M^+	166	Complex spectrum	32.43	1.6039	86.2757	8.5161	4.5987
Di Me B[a]A	28	256	34.06	M^+	170	$(M-15)^+$ present. Complex					
Tetra Me P	25	258	35.06	M^+	171	Complex spectrum					
B[a]P	29	252	35.38	M^+	172	Complex spectrum					
									1897.02	187.1959	101.0858

[a,b,c,d & e] See footnotes in Table 12.

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Table 16: PNA Compositional Analysis of CANMET Sample #5
(Acid-Base Cleaned Polyaromatic Fraction, Expt. I)

PNA Compound [a,b]	Peak[e] No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 42 Mass Spectrum in Appendix VI				Capillary GC - FID Analysis Chromatogram in Figure 35				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time[c]	PNA Content in Polyaromatic Fr. (µg/g)[d]	PNA Content in Distillation Residue b.p. >350°C (µg/g)[d]	PNA Content in crude oil/bitumen (µg/g)[d]
Tetra Me Naph	7	184	17.26	M^+	162	$(M-15)^+$ peak absent					
Phenanthrene	12	178	18.12	M^+	165	Spectrum similar to standard	17.46	0.8597	10.1658	1.0809	0.9696
Dimethylfluorene	2C	194	18.82	$(M-15)^+$	167	Strong M^+ peak at 194					
Dimethylfluorene	2D	194	19.32	$(M-15)^+$	171	Strong M^+ peak at 194	19.13	0.9419	2.4759	0.2632	0.2361
Penta Me Naph	8C	198	20.44	M^+	176	$(M-15)^+$ peak absent Mixture with Me Ph/A					
3 Me Ph	13	192	20.56	M^+	177	Spectrum similar to standard	19.98	0.9838	9.5966	1.0204	0.9153
Me Ph/Me A	13B	192	20.76	M^+	178	Complex spectrum Mixture					
2-Me A	13A	192	20.94	M^+	179)						
Me Ph/Me A	13C	192	21.06	M^+	180)	Spectrum similar to standard	20.37	1.0029	14.2110	1.5110	1.3554
Trimethylfluorene	3B	208	21.26	M^+	181	Strong $(M-15)^+$ peak at 193					
Trimethylfluorene	3C	208	21.68	$(M-15)^+$	184	Strong M^+ peak at 208					
Trimethylfluorene	3D	208	21.88	$(M-15)^+$	185	Strong M^+ peak at 208					
Hexa Me Naph	9C	212	22.44	M^+	187	Med. $(M-15)^+$ peak at 197	21.58	1.0625	1.9182	0.2039	0.1829
Hexa Me Naph	9D	212	22.56	M^+	188	Med. $(M-15)^+$ peak at 197					
Di Me Ph/Di Me A	14B	206	22.88	M^+	191	Med. strong $(M-15)^+$ peak at 191. Mixture.					
Di Me Ph/Di Me A	14D	206	23.18	M^+	192	Med. strong $(M-15)^+$ peak at 191. Mixture.	22.35	1.1004	3.4393	0.3657	0.3280
Di Me Ph/Di Me A	14E	206	23.26	M^+	193	Med. strong $(M-15)^+$ peak at 191. Mixture.					

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Table 16: PNA Compositional Analysis of CANMET Sample #5
(Acid-Base Cleaned Polyaromatic Fraction, Expt. 1)

...cont'd

PNA Compound [a,b]	Peak [c] No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 42 Mass Spectrum in Appendix VI				Capillary GC - FID Analysis Chromatogram in Figure 35				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time [c]	PNA Content in Polyaromatic Fr. [d] (µg/g)	PNA Content in Distillation Residue b.p. >350 C (µg/g) [d]	PNA Content in crude oil/bitumen (µg/g) [d]
Di Me Ph/Di Me A	14F	206	23.32	M^+	194	Strong $(M-15)^+$ peak at 191					
Di Me Ph/Di Me A	14G	206	23.50	M^+	195	Strong $(M-15)^+$ peak at 191 Complex'	22.85	1.1251	9.4587	1.0057	0.9021
Di Me Ph/Di Me A	14H	206	23.68	M^+	196	Mixture with Tetra Me Fl Complex	23.07	1.1359	11.0445	1.1743	1.0534
Tetramethylfluorene	4	222	23.82	$(M-15)^+$	197	Strong M^+ peak at 222					
Tetramethylfluorene	4A	222	23.94	M^+	198	Complex Spectrum					
Di Me Ph/Di Me A	14I	206	24.12	M^+	199	Strong $(M-15)^+$ peak at 191 Complex					
Tetramethylfluorene	4B	222	24.39	$(M-15)^+$	201	Strong M^+ peak at 222					
Pyrene	21A	202	24.50	M^+	202	Complex spectrum. Mixture					
Hepta Me Naph	10B	226	24.68	M^+	203	Strong $(M-15)^+$ peak					
Hepta Me Naph	10D	226	25.00	M^+	205	Complex spectrum	24.20	1.1915	3.8069	0.4047	0.3630
Hepta Me Naph	10E	226	25.12	M^+	206	Strong $(M-15)^+$ peak					
Tri Me Ph/Tri Me A	15A	220	25.32	M^+	207	Strong $(M-15)^+$ peak					
Tri Me Ph/Tri Me A	15B	220	25.50	M^+	208	Strong peak at $(M-15)^+$ Complex spectrum	24.57	1.2097	7.6310	0.8114	0.7278
Tri Me Ph/Tri Me A	15C	220	25.76	M^+	209	Strong $(M-15)^+$ peak	24.95	1.2284	11.9684	1.2725	1.1415
Me P/BFl	22A	216	25.88	M^+	210	Complex spectrum	25.25	1.2432	4.7387	0.5039	0.4520
Tri Me Ph/Tri Me A	15D	220	26.10	M^+	212	Strong $(M-15)^+$ peak					
Tri Me Ph/Tri Me A	15E	220	26.18	M^+	213	Strong $(M-15)^+$ peak					

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Table 16: PNA Compositional Analysis of CANMET Sample #5
(Acid-Base Cleaned Polyaromatic Fraction, Expt. 1)

...cont'd

PNA Compound [a] [b]	Peak [e] No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 42 Mass Spectrum in Appendix VI				Capillary GC - FID Analysis Chromatogram in Figure 35				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time [c]	PNA Content in [d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350 C (µg/g) [d]	PNA Content in crude oil/bitumen (µg/g) [d]
Tri Me Ph/Tri Me A	15F	220	26.32	M^+	214	Strong $(M-15)^+$ peak Complex spectrum					
Octa Me Naph	11A	240	26.56	M^+	215	Strong $(M-15)^+$ peak Complex spectrum					
Tri Me Ph/Tri Me A	15G	220	26.82	M^+	216	Strong $(M-15)^+$ peak					
Octa Me Naph	11B	240	26.94	M^+	217	Strong $(M-15)^+$ peak					
Me P/BFl	22E	216	27.12	M^+	218	Spectrum similar to standard	26.32	1.2959	12.5319	1.3324	1.1952
Octa Me Naph	11C	240	27.26	M^+	219	Strong $(M-15)^+$ peak					
Tetra Me Ph/Tetra Me A	16A	234	27.56	M^+	220	Strong $(M-15)^+$. Complex.	26.60	1.3097	5.9239	0.6299	0.5650
Octa Me Naph	11D	240	27.82	M^+	222	Strong $(M-15)^+$. Complex.	26.78	1.3186	3.3108	0.3519	0.3157
Tetra Me Ph/Tetra Me A	16B	234	28.00	M^+	223	Strong $(M-15)^+$ peak	27.13	1.3358	2.2764	0.1095	0.0982
Pentamethylfluorene	5	236	28.44	M^+	225	Complex spectrum Mixture	27.63	1.3604	4.4214	0.4701	0.4217
Di Me P	23A	230	28.76	M^+	226	Strong $(M-15)^+$ peak Complex spectrum					
Tetra Me Ph/Tetra Me A	16E	234	29.06	M^+	227	$(M-15)^+$ peak absent	27.98	1.3776	4.3884	0.4665	0.4185
Di Me P	23C	230	29.12	M^+	228	Complex spectrum					
Tetra Me Ph/Tetra Me A	16F	234	29.50	M^+	230	Complex spectrum	28.67	1.4116	3.3245	0.1480	0.1328
									126.6323	13.1259	11.7742

[a],[b],[c],[d] & [e] See footnotes in Table 12.

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Table 17: PNA Compositional Analysis of CANMET Sample #6
(Acid-Base Cleaned Polyaromatic Fraction, Expt. VI)

PNA Compound [a,b]	Peak No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 43 Mass Spectrum in Appendix VII				Capillary GC - FID Analysis Chromatogram in Figure 36				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time [c]	PNA Content in Polyaromatic Fr. (µg/g) [d]	PNA Content in Distillation Residue b.p. >350°C (µg/g) [d]	PNA Content in crude oil/bitumen (µg/g) [d]
Methylfluorene	1	180	16.00	$(M-15)^+$	46	Strong M^+ peak at 180	15.83	0.7915	21.7800	1.3010	0.4983
Methylfluorene	1A	180	16.12	$(M-15)^+$	47	Strong M^+ peak at 180	15.97	0.7985	119.8041	6.9339	2.6557
Phenanthrene	12	178	17.62	M^+	49	Spectrum similar to standard	17.47	0.8735	81.3049	4.8561	1.8599
Dimethylfluorene	2A	194	18.50	$(M-15)^+$	52	Strong M^+ peak at 194					
Dimethylfluorene	2B	194	18.68	$(M-15)^+$	53	Strong M^+ peak at 194	18.50	0.9250	44.8557	2.6791	1.0261
Dimethylfluorene	2C	194	18.82	$(M-15)^+$	54	Strong M^+ peak at 194	18.62	0.9310	54.0839	3.2303	1.2372
Dimethylfluorene	2D	194	19.39	$(M-15)^+$	56	Strong M^+ peak at 194					
Penta Me Naph	8A	198	19.56	M^+	57	$(M-15)^+$ peak absent					
3-Me Ph	13	192	20.00	M^+	58	Spectrum similar to standard					
2-Me A	13A	192	20.12	M^+	59	Spectrum similar to standard	20.00	1.0000	105.9602	6.3287	2.4239
Me Ph/Me A	13B	192	20.50	M^+	60	Spectrum similar to standard	20.40	1.0200	92.9882	5.5538	2.1271
Me Ph/Me A	13C	192	20.62	M^+	61	Mixture	20.48	1.0240	77.2916	4.6164	1.7681
Trimethylfluorene	3	208	20.88	$(M-15)^+$	62	Strong M^+ peak at 208					
Trimethylfluorene	3A	208	21.00	$(M-15)^+$	63	Strong M^+ peak at 208					
Hexa Me Naph	9	212	21.18	M^+	64	$(M-15)^+$ peak at 197					
Trimethylfluorene	3C	208	21.50	$(M-15)^+$	65	Strong M^+ peak at 208					
Hexa Me Naph	9A	212	21.62	M^+	66	$(M-15)^+$ peak absent. Mixture.	21.53	1.0765	40.4993	2.4188	0.9264
Trimethylfluorene	3D	208	21.88	$(M-15)^+$	67	Strong M^+ peak at 208					
Hexa Me Naph	9B	212	22.00	M^+	68	$(M-15)^+$ peak at 197					
Hexa Me Naph	9C	212	22.32	M^+	69	Strong $(M-15)^+$ peak at 197. Complex.					

CANMET PNA PROJECT
DAS-AC-ORF

Table 17: PNA Compositional Analysis of CANMET Sample #6
(Acid-Base Cleaned Polyaromatic Fraction, Expt. VI)

...cont'd

PNA Compound [a,b]	Peak [e] No.	Mol. Wt.	Capillary GC - MS Analysis Chromatogram in Figure 43 Mass Spectrum in Appendix VII				Capillary GC - FID Analysis Chromatogram in Figure 36				
			Ret. Time (min)	Base Peak	Spectrum No.	Remarks	Ret. Time (min)	Rel. Ret. Time [c]	PNA Content in [d] Polyaromatic Fr. (µg/g)	PNA Content in Distillation Residue b.p. >350°C (µg/g) [d]	PNA Content in crude oil/bitumen (µg/g) [d]
Di Me Ph/Di Me A	14A	206	22.76	M^+	70	Strong $(M-15)^+$ peak at 191	22.68	1.1340	79.5949	4.7540	1.8208
Di Me Ph/Di Me A	14B	206	22.88	M^+	71	Strong $(M-15)^+$ peak at 191	22.88	1.1440	76.0648	4.5431	1.7400
Di Me Ph/Di Me A	14C	206	22.94	M^+	72	Strong $(M-15)^+$ peak at 191	23.08	1.1540	48.7098	2.9091	1.1142
Di Me Ph/Di Me A	14D	206	23.18	M^+	74	Strong $(M-15)^+$ peak at 191	23.33	1.1665	13.4993	0.8063	0.3088
Di Me Ph/Di Me A	14F	206	23.38	M^+	75	Strong $(M-15)^+$ peak at 191					
Di Me Ph/Di Me A	14H	206	23.62	M^+	76	Strong $(M-15)^+$ peak at 191					
Hepta Me Naph	10A	226	24.26	M^+	78	Strong $(M-15)^+$ peak at 211	24.21	1.2105	21.5140	1.2848	0.4921
Hepta Me Naph	10B	226	24.56	M^+	79	Strong $(M-15)^+$ peak at 211	24.52	1.2260	18.5920	1.1104	0.4253
Tri Me Ph/Tri Me A	15	220	24.94	M^+	81	Strong $(M-15)^+$ peak at 205	24.95	1.2475	57.5214	3.4355	1.3158
Tri Me Ph/Tri Me A	15A	220	25.26	M^+	83	Strong $(M-15)^+$ peak at 205	25.25	1.2625	26.8277	1.6023	0.6137
Tri Me Ph/Tri Me A	15E	220	26.26	M^+	86	Strong $(M-15)^+$ peak at 205	26.30	1.3150	32.3991	1.9350	0.7411
Tetra Me Ph/Tetra Me A	16	234	27.12	M^+	88	Strong $(M-15)^+$ at 219. Complex.					
Tetra Me Ph/Tetra Me A	16A	234	27.50	M^+	90	Strong $(M-15)^+$ at 219					
									1013.24	60.2986	23.0445

a,b,c,d & e See footnotes in Table 12.

CANMET PNA PROJECT
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Table 18: PNA in CANMET Sample No. 1 Acid-Base Cleaned and μ-Styragel -μSpherogel Fractionated Polyaromatic Fraction (Expt. IX) Tentative Characterization by Capillary GC-MS (see Chromatogram in Fig. 45 and Mass Spectrum in Appendix IIA)

PNA Compound[(a)&(b)]	Molecular Wt	Base Peak	Spectrum No.
Phenanthrene/Anthracene	178	M^+	196
Me Ph/Me A	192	M^+	204
Me Ph/Me A	192	M^+	206
Hexa Me Naph	212	M^+	208
Hexa Me Naph	212	M^+	209
Hexa Me Naph	212	M^+	210
Hexa Me Naph	212	M^+	211
Hexa Me Naph	212	M^+	212
Di Me Ph/Di Me A	206	M^+	213
Di Me Ph/Di Me A	206	M^+	215
Hepta Me Naph	226	M^+	217
Di Me Ph/Di Me A	206	$(M-15)^+$	219
Di Me Ph/Di Me A	226	M^+	220
Di Me Ph/Di Me A	226	M^+	221
Di Me Ph/Di Me A	226	M^+	222
Di Me Ph/Di Me A	226	M^+	223
Di Me Ph/Di Me A	226	M^+	224
Tri Me Ph/Tri Me A	220	M^+	225
Tri Me Ph/Tri Me A	220	M^+	226
Tri Me Ph/Tri Me A	220	M^+	227
Tri Me Ph/Tri Me A	220	M^+	228

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Table 18: PNA in CANMET Sample No. 1 Acid-Base Cleaned and μ-Styragel -μSpherogel Fractionated Polyaromatic Fraction (Expt. IX) Tentative Characterization by Capillary GC-MS (see Chromatogram in Fig. 45 and Mass Spectrum in Appendix 11A)

PNA Compound[(a)&(b)]	Molecular Wt	Base Peak	Spectrum No.
Octa Me Naph	240	$(M-15)^+$	230
Tri Me Ph/Tri Me A	220	M^+	231
Tri Me Ph/Tri Me A	220	M^+	232
Me Py	216	M^+	233
Tetra Me Ph/A	234	M^+	234
Tetra Me Ph/A	234	M^+	235
Tetra Me Ph/A	234	M^+	236
Penta Me Fl	236	M^+	237
Tetra Me Ph/A	234	M^+	240
Hexa Me Fl	250*	M^+	241
Hexa Me Fl	250*	M^+	242
Penta Me Ph/A	248	M^+	243
Penta Me Ph/A	248	M^+	246
Penta Me Ph/A	248	M^+	247
Hepta Me Ph/A	276	M^+	253

(a) See Footnotes in Table 22.

(b) For comparison, see Table 12.

* Not detected in acid-base cleaned polyaromatic fraction of Sample 1 (Expt. X) which was not cleaned by molecular size fractionation.

CANMET PNA PROJECT
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Table 19: PNA in CANMET Sample No. 3 Acid-Base Cleaned and μ-Styragel -μSpherogel Fractionated Polyaromatic Fraction (Expt. XI) Tentative Characterization by Capillary GC-MS (see Chromatogram in Fig. 46 and Mass Spectrum in Appendix IVA)

PNA Compound[(a)&(b)]	Molecular Wt.	Base Peak	Spectrum No.
Me Fl	180	$(M-15)^+$	258
Me Fl	180	$(M-15)^+$	259
?	184*	M^+	261
?	184*	M^+	262
Ph/A	178	M^+	263
Ph/A	178	M^+	264
Me Fl	180	$(M-15)^+$	266
Di Me Fl	194	$(M-15)^+$	267
Di Me Fl	194	$(M-15)^+$	268
Di Me Fl	194	$(M-15)^+$	269
Di Me Fl	194	$(M-15)^+$	270
Di Me Fl	194	$(M-15)^+$	271
Penta Me Naph	198	M^+	272
Di Me Fl	194	$(M-15)^+$	274
Penta Me Naph	198	M^+	275
Penta Me Naph	198	M^+	276
Penta Me Naph	198	M^+	277
Me Ph/Me A	192	M^+	278
Me Ph/Me A	192	M^+	279
Me Ph/Me A	192	M^+	280
Me Ph/Me A	192	M^+	281
Di Me Fl	194	$(m-15)^+$	282

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Table 19: PNA in CANMET Sample No. 3 Acid-Base Cleaned and μ-Styragel -μSpherogel Fractionated Polyaromatic Fraction (Expt. XI) Tentative Characterization by Capillary GC-MS (see Chromatogram in Fig. 46 and Mass Spectrum in Appendix IVA)

...cont'd

PNA Compound(a)&(b)	Molecular Wt.	Base Peak	Spectrum No.
Tri Me Fl	208	$(M-15)^+$	283
Hexa Me Naph	212	M^+	284
Hexa Me Naph	212	M^+	285
Hexa Me Naph	212	M^+	286
Hexa Me Naph	212	M^+	287
Hexa Me Naph	212	M^+	288
Hexa Me Naph	212	M^+	289
Hexa Me	212	M^+	290
Hexa Me	212	M^+	291
Hexa Me	212	M^+	292
Di Me Ph/A	206	$(M-15)^+$	293
Hexa Me Naph	212	M^+	294
Di Me Ph/A	206	M^+	295
Di Me Ph/A	206	M^+	296
Di Me Ph/A	206	M^+	298
Hexa Me Naph	212	M^+	298
Tetra Me Fl	222	$(M-15)^+$	300
Di Me Ph/A	206	M^+	301
Hepa Me Naph	226	M^+	302
Hepa Me Naph	226	M^+	303
Hepa Me Naph	226	M^+	304
Hepa Me Naph	226	M^+	305
Hepa Me Naph	226	M^+	306

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Table 19: PNA in CANMET Sample No. 3 Acid-Base Cleaned and μ-Styragel -μSpherogel Fractionated Polyaromatic Fraction (Expt. XI) Tentative Characterization by Capillary GC-MS (see Chromatogram in Fig. 46 and Mass Spectrum in Appendix IVA)

...cont'd

PNA Compound[(a)&(b)]	Molecular Wt.	Base Peak	Spectrum No.
Tri Me Ph/A	220	M^+	307
Tri Me Ph/A	220	M^+	308
Tri Me Ph/A	220	M^+	309
Octa Me Naph	240	$(M-15)^+$	311
Tri Me Ph/A	220	M^+	313
?	246*	$(M-15)^+$	314
Octa Me Naph	240	M^+	316
Tetra Me Ph/A	234	M^+	317
Hexa Me Fl	250	M^+	320

(a) See Footnotes in Table 22.

(b) For comparison, see Table 14.

*Not detected in acid-base cleaned polyaromatic fraction of Sample #3 (Expt. XII) which was not cleaned by molecular size fractionation.

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Table 20: PNA in CANMET Sample No. 5 Acid-Base Cleaned and μ-Styragel -μSpherogel Fractionated Polyaromatic Fraction (Expt. III) Tentative Characterization by Capillary GC-MS (see Chromatogram in Fig. 47 and Mass Spectrum in Appendix VIA)

PNA Compound[(a)&(b)]	Molecular Wt	Base Peak	Spectrum No.
Tetra Me Naph	184	M^+	24
Ph/A	178	M^+	25
Di Me Fl	194	$(M-15)^+$	28
Di Me Fl	194	$(M-15)^+$	29
Di Me Fl	194	$(M-15)^+$	30
Di Me Fl	194	$(M-15)^+$	32
Penta Me Naph	198	M^+	33
Penta Me Naph	198	M^+	34
Me A/Me Ph	192	M^+	35
Me A/Me Ph	192	M^+	36
Penta Me Naph	198	M^+	37
Me Ph/Me A	192	M^+	38
Me Ph/Me A	192	M^+	39
Tri Me Fl	208	$(M-15)^+$	40
Hexa Me Naph	212	M^+	41
Tri Me Fl	208	$(M-15)^+$	42
Tri Me Fl	208	M^+	43
Tri Me Fl	208	$(M-15)^+$	44
Hexa Me Naph	212	M^+	45
Di Me Ph/A	206	M^+	47
Di Me Ph/A	206	M^+	48
Di Me Ph/A	206	M^+	49
Di Me Ph/A	206	M^+	50
Di Me Ph/A	206	M^+	51

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Table 20: PNA in CANMET Sample No. 5 Acid-Base Cleaned and μ-Styragel -μSpherogel Fractionated Polyaromatic Fraction (Expt. III) Tentative Characterization by Capillary GC-MS (see Chromatogram in Fig. 47 and Mass Spectrum in Appendix VIA)

...cont'd

PNA Compound[(a)&(b)]	Molecular Wt	Base Peak	Spectrum No.
Tetra Me Fl	222	$(M-15)^+$	52
Tri Me Fl	208	M^+	53
Hepta Me Naph	226	M^+	54
Hepta Me Naph	226	M^+	55
Hepta Me Naph	226	M^+	56
Tri Me Ph/A	220	M^+	57
Tri Me Ph/A	220	M^+	58
Tri Me Ph/A	220	M^+	59
Tri Me Ph/A	220	$(M-15)^+$	61
Tri Me Ph/A	220	M^+	62
?	238*	M^+	63
Octa Me Naph	240	M^+	64
Tri Me Ph/A	220	M^+	65
Octa Me Naph	240	M^+	66
Me Py/BF	216	M^+	67
Octa Me Naph	240	$(M-15)^+$	69
?	232*	$(M-15)^+$	70
Tetra Me Ph/A	234	M^+	71
Penta Me Fl	236	M^+	72
Hexa Me Fl	250*	M^+	73

(a) See Footnotes in Table 22.

(b) For comparison, see Table 16.

* Not detected in acid-base cleaned polyaromatic fraction of Sample #5 (Expt. I) which was not cleaned by molecular size fractionation.

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Table 21: PNA in CANMET Sample No. 6 Acid-Base Cleaned and μ-Styragel -μSpherogel Fractionated Polyaromatic Fraction (Expt. VII) Tentative Characterization by Capillary GC-MS (see Chromatogram in Fig. 48 and Mass Spectrum in Appendix VIIA)

PNA Compound[(a)&(b)]	Molecular Wt	Base Peak	Spectrum No.
Me Fluorene	180	$(M-15)^+$	141
?	196*	M^+	143
Phenanthrene/Anthracene	178	M^+	144
Me Fluorene	180	$(M-15)^+$	145
Di Me Fluorene	194	$(M-15)^+$	146
Di Me Fluorene	194	$(M-15)^+$	147
Di Me Fluorene	194	$(M-15)^+$	148
Di Me Fluorene	194	$(M-15)^+$	149
Penta Me Naph	198	M^+	150
Me Ph/Me A	192	M^+	151
Me Ph/Me A	192	M^+	152
Me Ph/Me A	192	M^+	153
Me Ph/Me A	192	M^+	154
Tri Me Fluorene	208	$(M-15)^+$	155
Hexa Me Naph	212	M^+	156
Tri Me Fluorene	208	M^+	157
Hexa Me Naph	212	M^+	158
Tri Me Fluorene	208	$(M-15)^+$	159
Hexa Me Naph	212	M^+	160

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Table 21: PNA in CANMET Sample No. 6 Acid-Base Cleaned and μ-Styragel -μSpherogel Fractionated Polyaromatic Fraction (Expt. VII) Tentative Characterization by Capillary GC-MS (see Chromatogram in Fig. 48 and Mass Spectrum in Appendix VIIA)

...cont'd

PNA Compound(a)&(b)	Molecular Wt	Base Peak	Spectrum No.
Di Me Ph/Di Me A	206	M^+	161
Di Me Ph/Di Me A	206	M^+	162
Di Me Ph/Di Me A	206	M^+	163
Di Me Ph/Di Me A	206	M^+	164
Tetra Me Fluorene	222*	$(M-15)^+$	165
?	218*	M^+	168
Hepta Me Naph	226	M^+	170
Tri Me Ph/A	220	M^+	172

(a) See Footnotes in Table 22.

(b) For comparison, see Table 17.

* Not detected in acid-base cleaned polyaromatic fraction of Sample #6 (Expt. VI) which was not cleaned by molecular size fractionation.

CANMET PNA PROJECT
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Table 22: Summary of Work on Characterization of PNA in CANMET Samples*

PNA Compound	Mol. Wt.	Peak No.**	Sample Identification					
			CANMET #1	CANMET #2	CANMET #3	CANMET #4	CANMET #5	CANMET #6
Alkyl Fluorenes								
Methylfluorene(a)	180	1				✓		✓
Methylfluorene	180	1A			✓	✓		✓
Ethylfluorene	194	2			✓			
Dimethylfluorene(f)	194	2A			✓	✓		✓
Dimethylfluorene	194	2B			✓	✓		✓
Dimethylfluorene	194	2C			✓	✓	✓	✓
Dimethylfluorene	194	2D			✓	✓	✓	✓
Trimethylfluorene(b)	208	3			✓			✓
Trimethylfluorene	208	3A			✓	✓		✓
Trimethylfluorene	208	3B	✓		✓		✓	
Trimethylfluorene	208	3C			✓		✓	✓
Trimethylfluorene	208	3D			✓	✓	✓	✓
Trimethylfluorene	208	3E				✓		
Tetramethylfluorene(c)	222	4					✓	
Tetramethylfluorene	222	4A			✓		✓	
Tetramethylfluorene	222	4B					✓	
Pentamethylfluorene	236	5	✓				✓	
Hexamethylfluorene	250	6			✓			
Hexamethylfluorene	250	6A			✓			

CANMET PNA PROJECT
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Table 22: Summary of Work on Characterization of PNA in CANMET Samples*

...cont'd

PNA Compound	Mol. Wt.	** Peak No.	Sample Identification					
			CANMET #1	CANMET #2	CANMET #3	CANMET #4	CANMET #5	CANMET #6
Alkyl Naphthalenes								
TetraMeNaph (c)	184	7				✓	✓	
PentaMeNaph	198	8	✓					
PentaMeNaph	198	8A			✓	✓		✓
PentaMeNaph	198	8B	✓		✓			
PentaMeNaph	198	8C					✓	
HexaMeNaph	212	9			✓			✓
HexaMeNaph	212	9A	✓		✓			✓
HexaMeNaph	212	9B	✓		✓			✓
HexaMeNaph	212	9C	✓		✓		✓	✓
HexaMeNaph	212	9D			✓		✓	
HeptaMeNaph (m)	226	10	✓					
HeptaMeNaph	226	10A	✓		✓	✓		✓
HeptaMeNaph	226	10B	✓	✓	✓	✓	✓	✓
HeptaMeNaph	226	10C	✓		✓			
HeptaMeNaph	226	10D	✓				✓	
HeptaMeNaph	226	10E					✓	
OctaMeNaph (k)	240	11			✓			
OctaMeNaph	240	11A			✓		✓	
OctaMeNaph	240	11B	✓				✓	
OctaMeNaph	240	11C	✓	✓	✓		✓	
OctaMeNaph	240	11D					✓	

CANMET PNA PROJECT
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Table 22: Summary of Work on Characterization of PNA in CANMET Samples*

...cont'd

PNA Compound	Mol. Wt.	** Peak No.	Sample Identification					
			CANMET #1	CANMET #2	CANMET #3	CANMET #4	CANMET #5	CANMET #6
Phenanthrene (Ph), Anthracene (A) and Alkyl Derivatives								
Phenanthrene	178	12			✓	✓	✓	✓
Anthracene	178	12A	✓			✓		
3MePh	192	13	✓		✓	✓	✓	✓
2MeA	192	13A	✓		✓	✓	✓	✓
MePh/MeA	192	13B	✓		✓	✓	✓	✓
MePh/MeA	192	13C	✓				✓	✓
DiMePh/DiMeA	206	14				✓		
DiMePh/DiMeA	206	14A			✓	✓		✓
DiMePh/DiMeA	206	14B	✓		✓	✓	✓	✓
DiMePh/DiMeA	206	14C			✓	✓		✓
DiMePh/DiMeA	206	14D	✓		✓		✓	✓
DiMePh/DiMeA	206	14E	✓				✓	
DiMePh/DiMeA	206	14F	✓		✓		✓	✓
DiMePh/DiMeA	206	14G	✓	✓	✓		✓	
DiMePh/DiMeA	206	14H	✓		✓		✓	✓
DiMePh/DiMeA	206	14I			✓		✓	
TriMePh/TriMeA(b)	220	15			✓	✓		✓
TriMePh/TriMeA	220	15A	✓	✓	✓		✓	✓
TriMePh/TriMeA	220	15B	✓	✓	✓	✓	✓	
TriMePh/TriMeA	220	15C	✓	✓	✓		✓	
TriMePh/TriMeA	220	15D	✓		✓		✓	

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Table 22: Summary of Work on Characterization of PNA in CANMET Samples*

...cont'd

PNA Compound	Mol. Wt.	** Peak No.	Sample Identification					
			CANMET #1	CANMET #2	CANMET #3	CANMET #4	CANMET #5	CANMET #6
TriMePh/TriMeA	220	15E	✓		✓		✓	✓
TriMePh/TriMeA	220	15F	✓		✓		✓	
TriMePh/TriMeA	220	15G	✓				✓	
TetraMePh/TetraMeA(c)	234	16						✓
TetraMePh/TetraMeA	234	16A	✓		✓	✓	✓	✓
TetraMePh/TetraMeA	234	16B	✓	✓	✓	✓	✓	
TetraMePh/TetraMeA	234	16C	✓					
TetraMePh/TetraMeA	234	16D			✓	✓		
TetraMePh/TetraMeA	234	16E	✓	✓	✓	✓	✓	
TetraMePh/TetraMeA	234	16F					✓	
PentaMePh/PentaMeA	248	17			✓	✓		
PentaMePh/PentaMeA	248	17A	✓	✓		✓		
PentaMePh/PentaMeA	248	17B				✓		
PentaMePh/PentaMeA	248	17C	✓					
HexaMePh/HexaMeA	262	18		✓				
HexaMePh/HexaMeA	262	18A		✓				
HeptaMePh/HeptaMeA(1)	276	19	✓	✓				
HeptaMePh/HeptaMeA	276	19A	✓	✓				
OctaMePh/OctaMeA	290	20	✓					
OctaMePh/OctaMeA	290	20A	✓					

CANMET PNA PROJECT
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Table 22: Summary of Work on Characterization of PNA in CANMET Samples*

...cont'd

PNA Compound	Mol. Wt.	** Peak No.	Sample Identification					
			CANMET #1	CANMET #2	CANMET #3	CANMET #4	CANMET #5	CANMET #6
Pyrene (P), Fluoranthene, Benzofluorene (BFL), and Alkyl Derivatives								
Fluoranthene	202	21				✓		
Pyrene	202	21A				✓	✓	
MeP(e)/BFl	216	22				✓		
MeP/BFl	216	22A				✓	✓	
MeP/BFl	216	22B				✓		
4-MeP/BFl	216	22C				✓		
3-MeP, 1-MeP/BFl	216	22D			✓			
MeP/BFl	216	22E	✓				✓	
DiMeP(d, e, f)	230	23				✓		
DiMeP	230	23A				✓		
DiMeP	230	23B					✓	
DiMeP	230	23C					✓	
DiMeP	230	23D	✓					
TriMeP(e, b)	244	24				✓		
TetraMeP(e, c)	258	25				✓		

CANMET PNA PROJECT
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Table 22: Summary of Work on Characterization of PNA in CANMET Samples*

...cont'd

PNA Compound	Mol. Wt.	** Peak No.	Sample Identification					
			CANMET #1	CANMET #2	CANMET #3	CANMET #4	CANMET #5	CANMET #6
Benzo[a]A and Alkyl Derivatives and B[a]P								
B[a]A(g)	228	26				✓		
MeB[a]A(h)	242	27				✓		
DiMeB[a]A(h)	256	28				✓		
B[a]P	252	29				✓		
Cyclopentenophen and Alkyl Derivatives								
Cyclopentenoph (CPPh)(i)	204	30				✓		
MeCPPh(j)	218	31				✓		
MeCPPh	218	31A				✓		
MeCPPh	218	31B				✓		
DiMeCPPh	232	32			✓	✓		
DiMeCPPh	232	32A	✓					
DiMeCPPh	232	32B				✓		
DiMeCPPh	232	32C				✓		

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Footnotes

(a) Could be dimethylacenaphthylene.

(b) Could be ethylmethyl-, trimethyl- or propyl.

(c) Could be diethyl-, ethyl dimethyl-, tetramethyl-, methyl propyl- or butyl-.

(d) Could be alkyl benzofluorene derivative.

(e) Could be pyrene or fluoranthene.

(f) Could be dimethyl or ethyl.

(g) Could be chrysene, triphenylene or benzo{c}phenanthrene.

(h) Could be a derivative of chrysene.

(i) Could be phenylnaphthalene or dihydropyrene.

(j) Could be benzylnaphthalene or dihydromethylpyrene.

(k) Could be methylbenz{ghi}fluoranthene (strong {M-15} peak is present).

(l) Could not be O-pheylene pyrene or benz{ghi}perylene, since a strong {M-15} peak is present, and these two PNA have retention time much higher than heptaMePh/heptaMeA.

(m) Could not be benz{ghi}fluoranthene, since strong {M-15} peak is present.

* Tentative identification by capillary GC-MS.

** Numbers refer to peaks in GC chromatograms.

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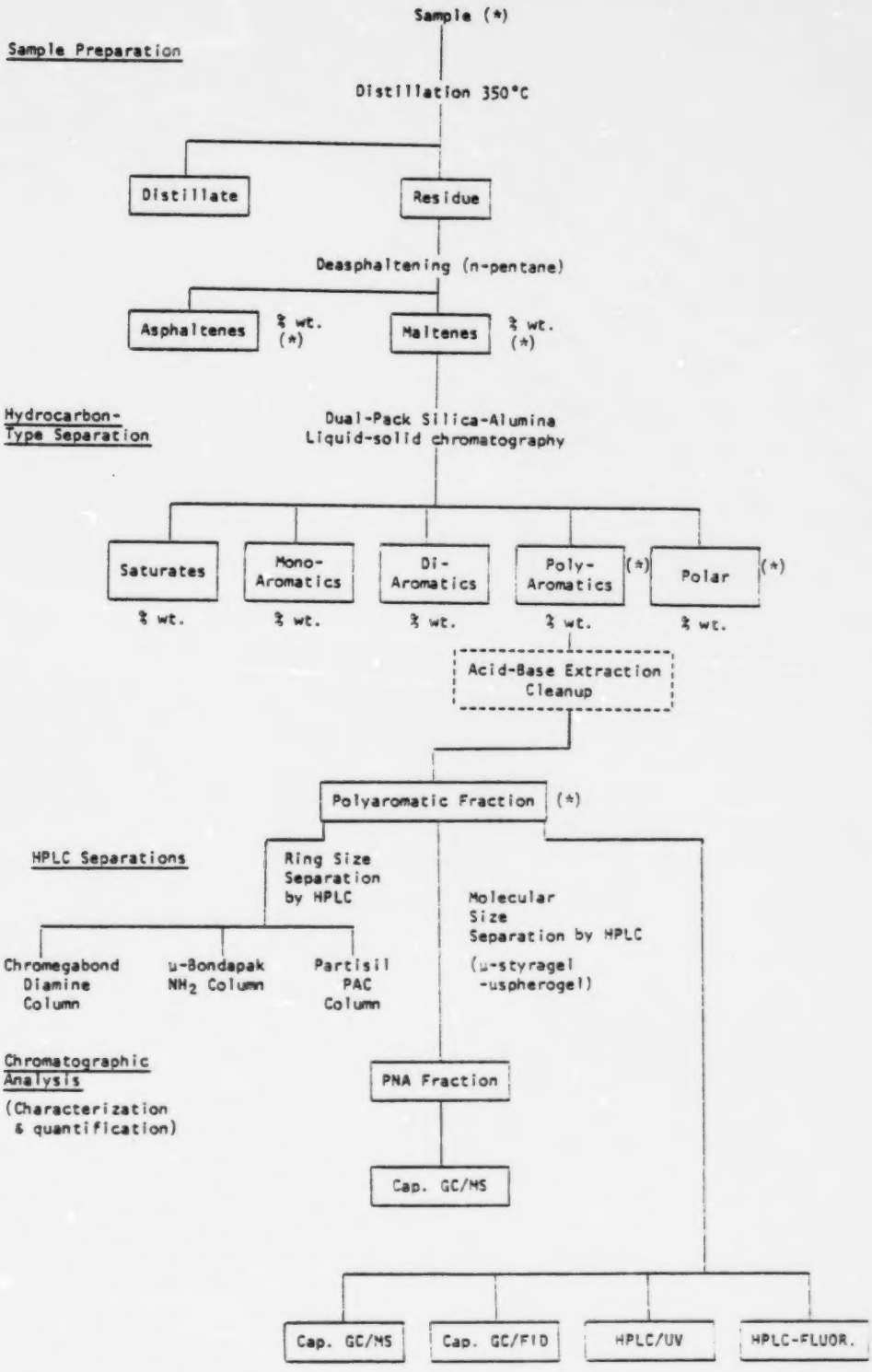
FIGURES

(Figures 1 - 48)



(*)Elemental Analysis:
C, H, N, S.

FIGURE 1: Fractionation and Analytical Scheme for Characterization of PNA

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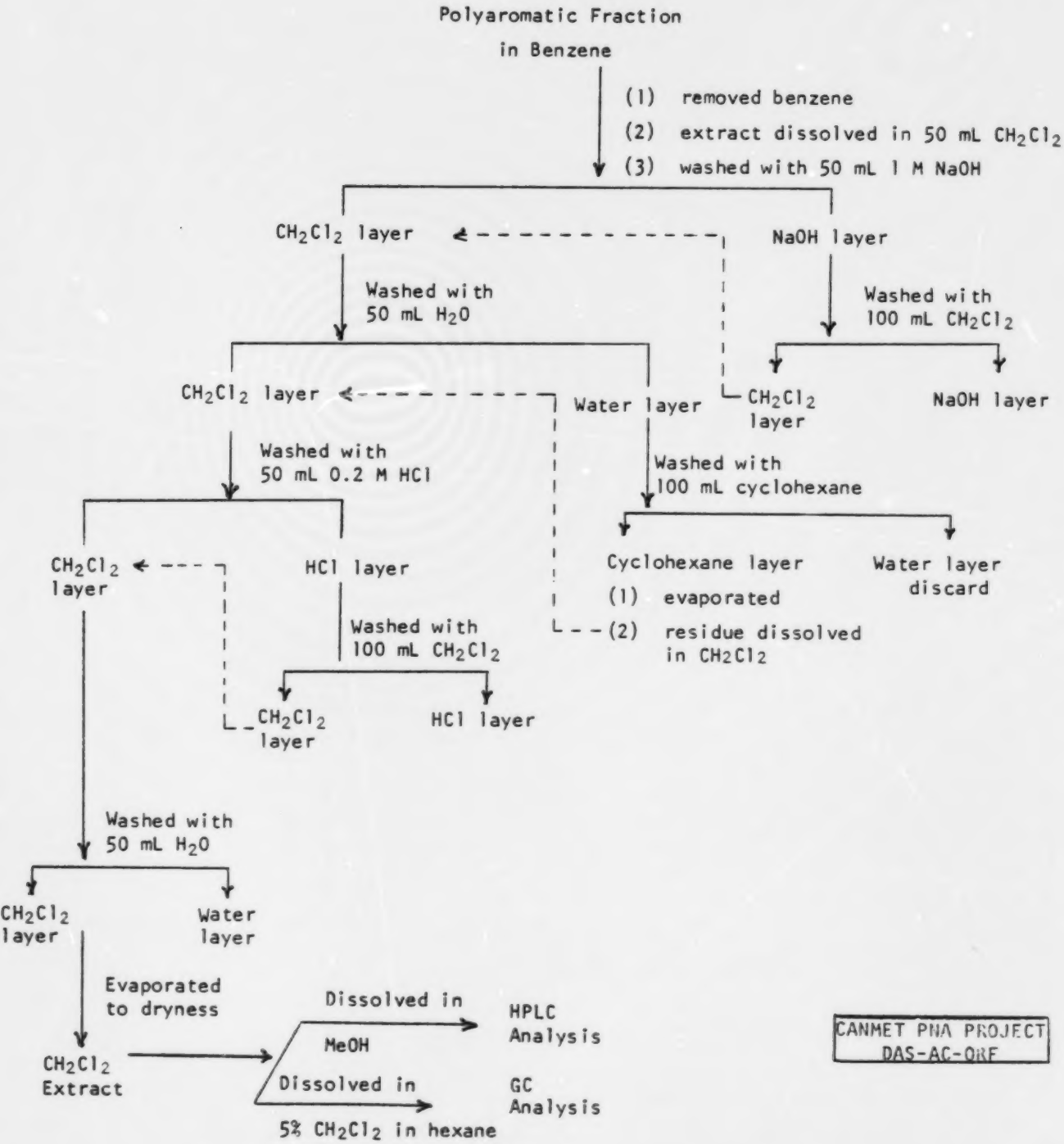
Figure: 2

Acid-Base Extraction Cleanup Scheme of Benzene Polyaromatic Fractions



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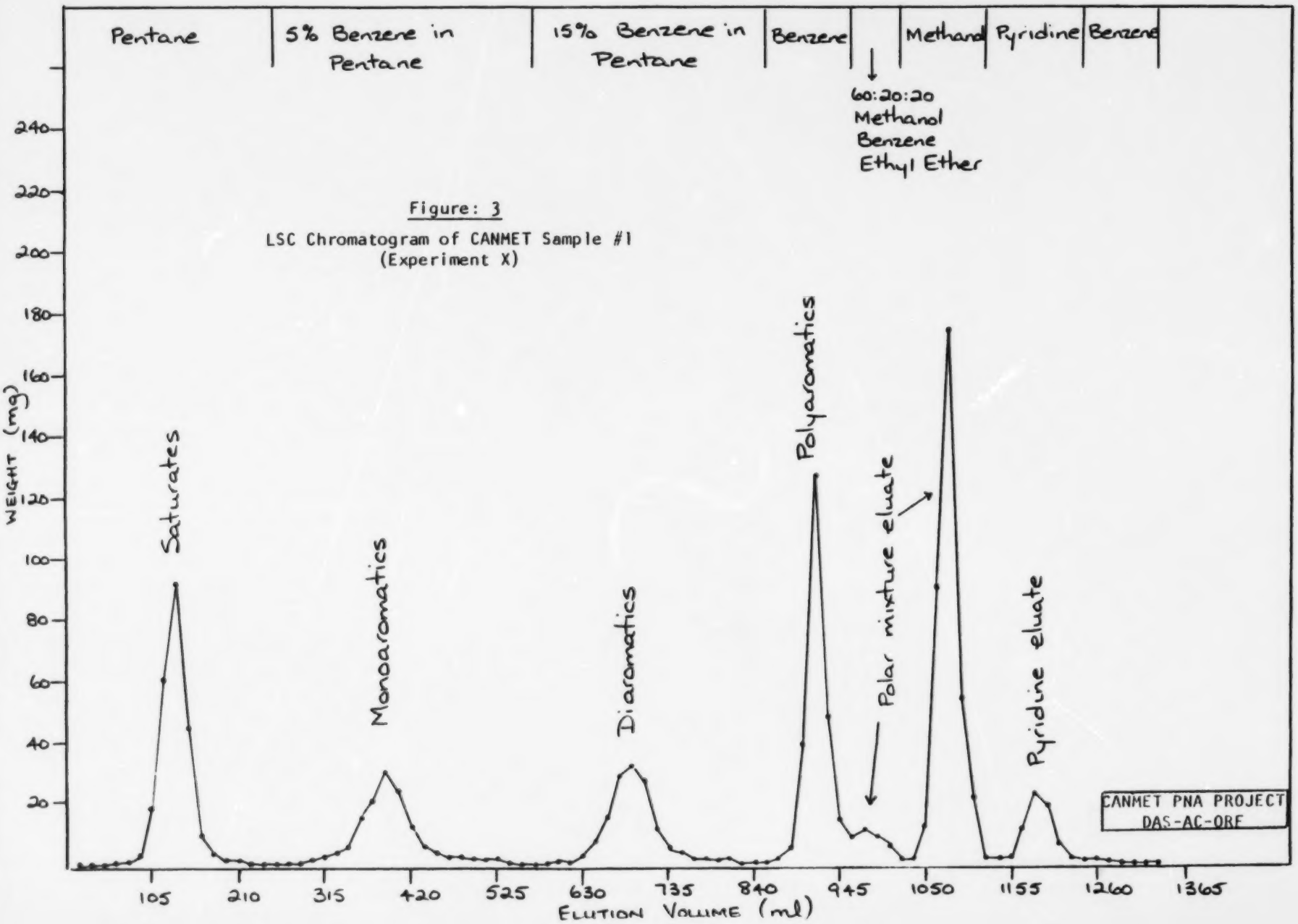


Figure: 3

LSC Chromatogram of CANMET Sample #1
(Experiment X)

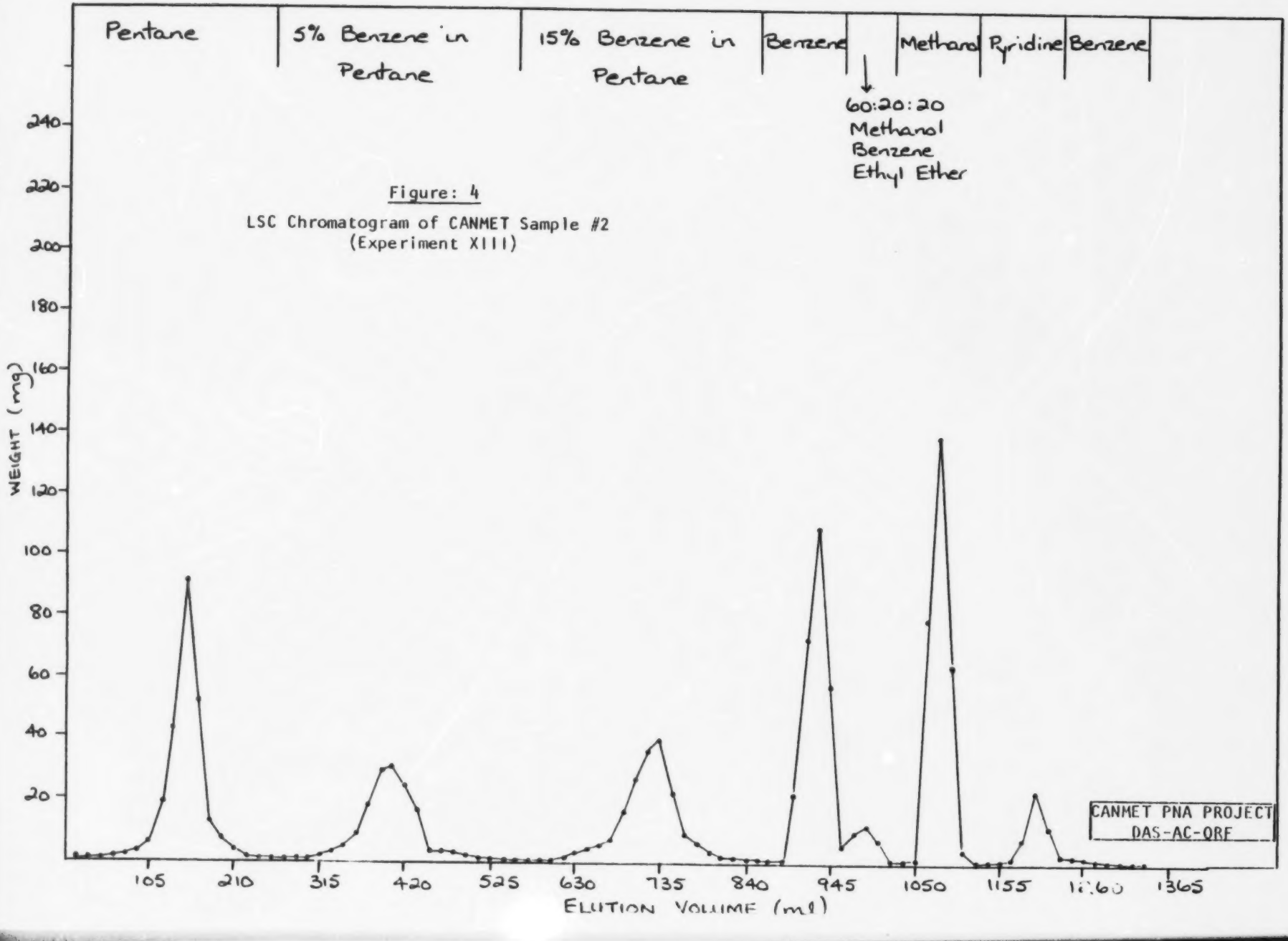


Figure: 4

LSC Chromatogram of CANMET Sample #2
(Experiment XIII)

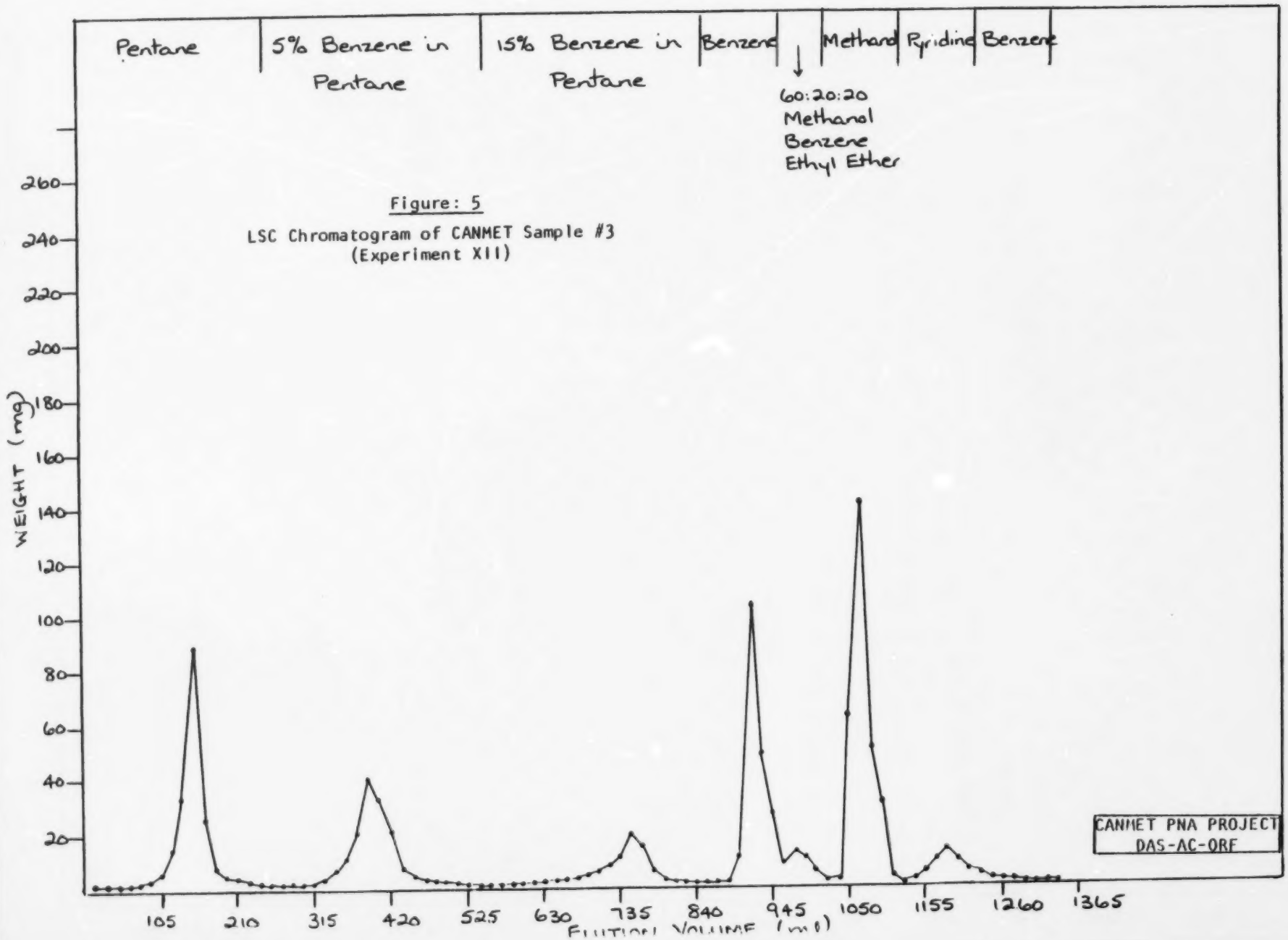


Figure: 5

LSC Chromatogram of CANMET Sample #3
(Experiment XII)

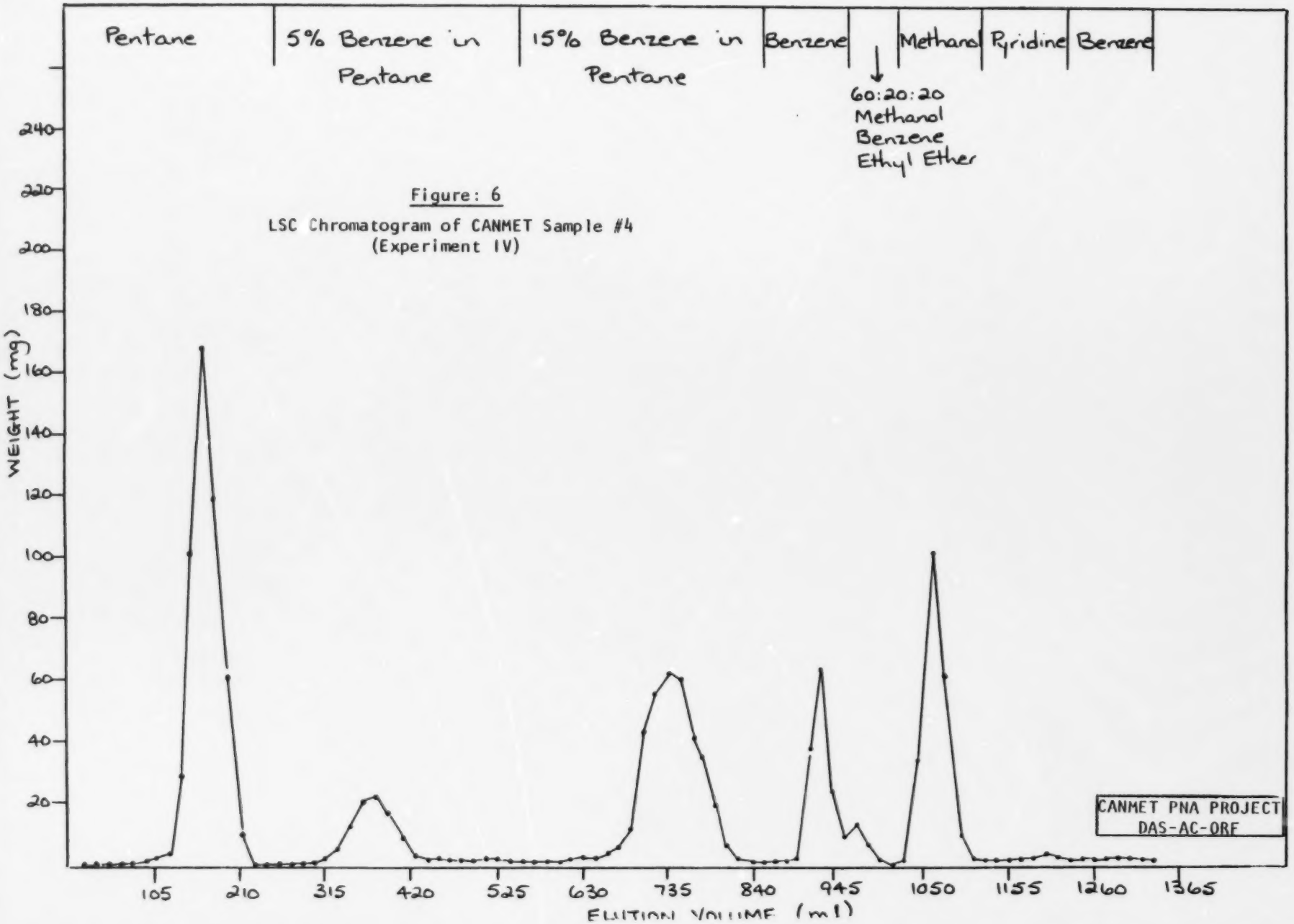


Figure: 6

LSC Chromatogram of CANMET Sample #4
(Experiment IV)

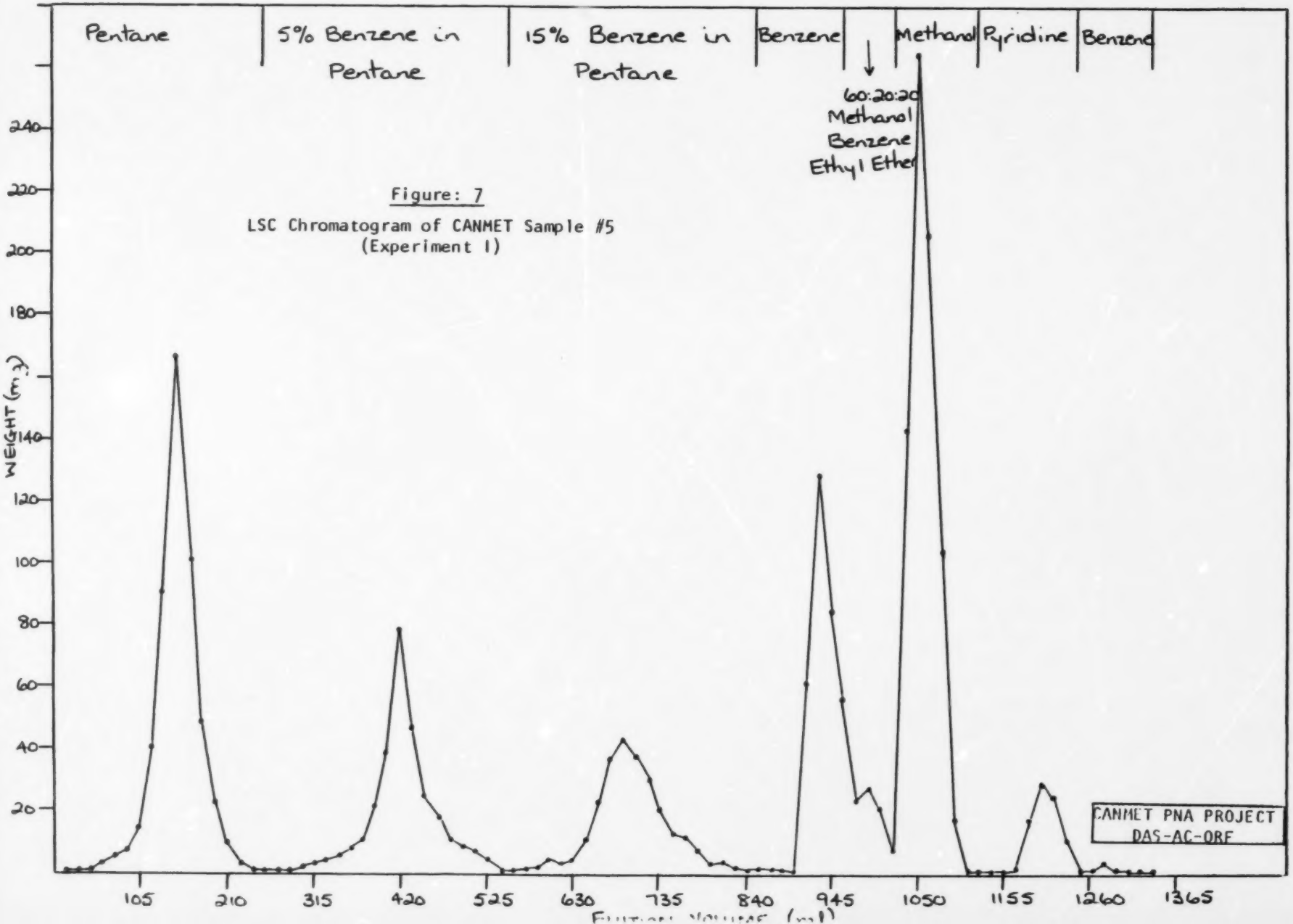


Figure: 7

LSC Chromatogram of CANMET Sample #5
(Experiment I)

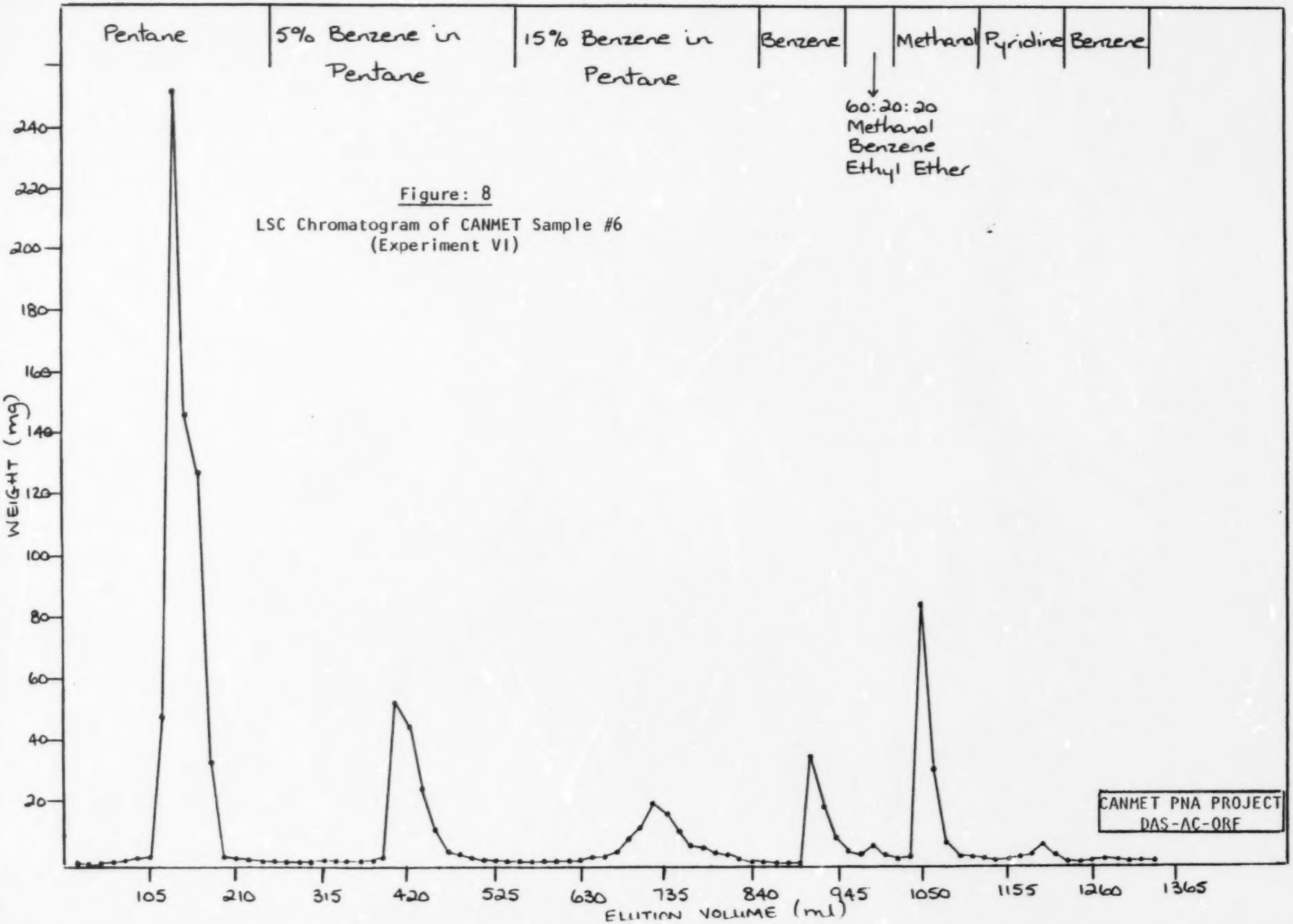
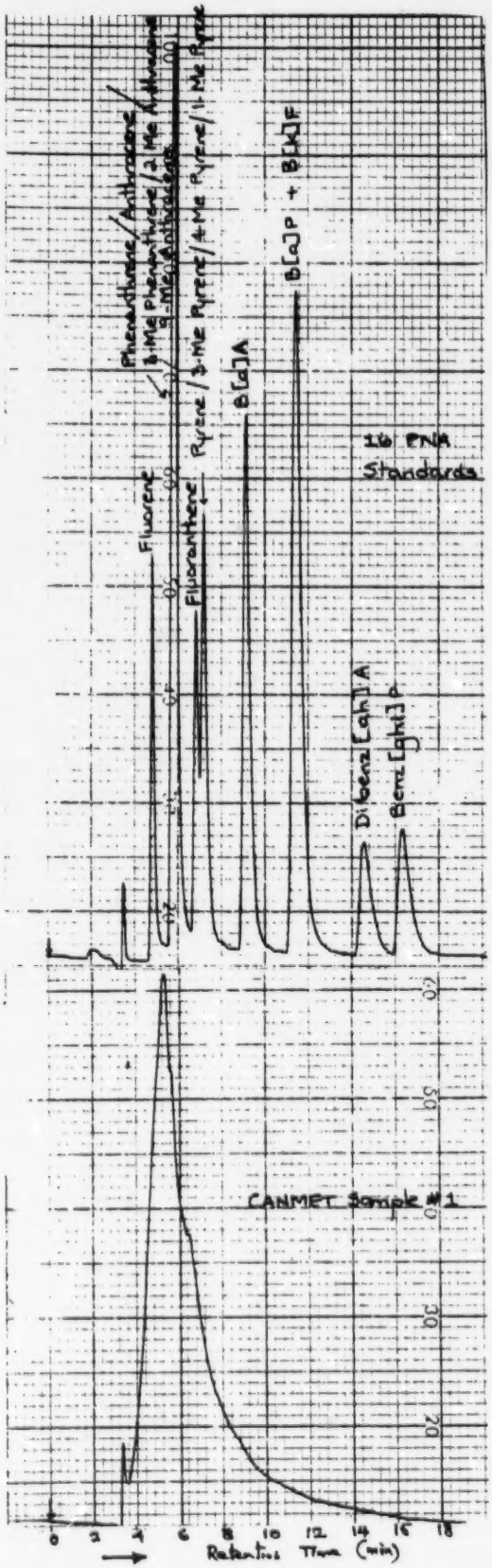


Figure: 8

LSC Chromatogram of CANMET Sample #6
(Experiment VI)

Figure: 9

HPLC Chromatograms of 16 PNA Standards and Polyaromatic Fractions of Sample #1 (Experiment X), Sample #2 (Experiment XIII) and Sample #3 (Experiment XII) - Ring Size Separation in Chromegabond Diamine (see Conditions in Table 3 and Concentrations in Table 5A)



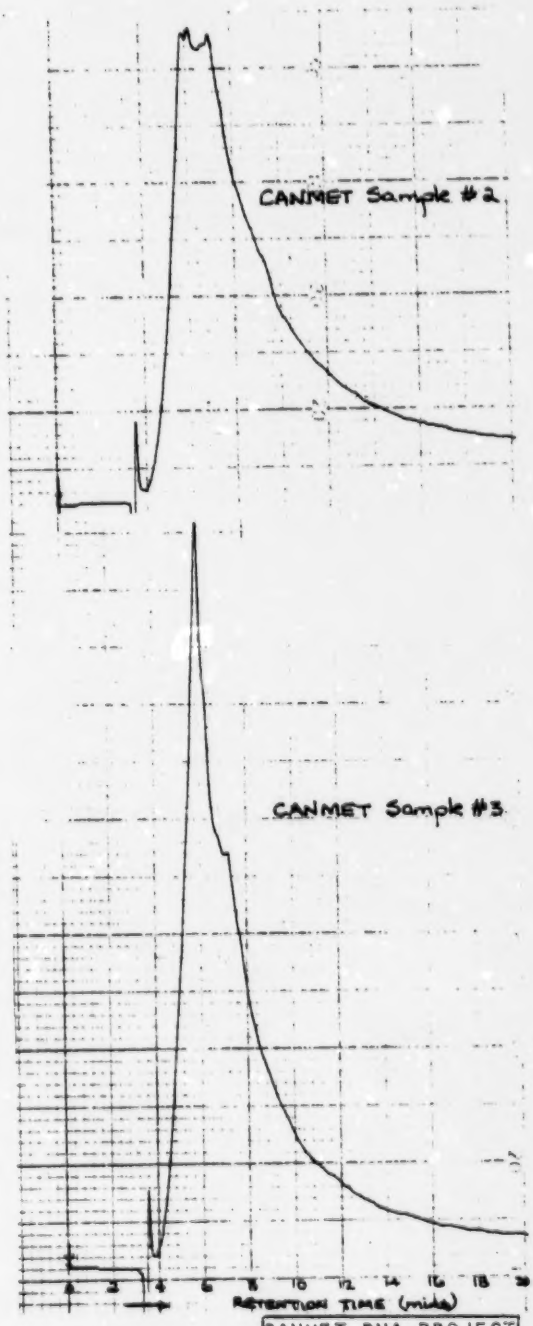


Figure: 10

HPLC Chromatograms of 16 PNA Standards and Polyaromatic Fractions of Sample #4 (Experiment IV), Sample #5 (Experiment I) and Sample #6 (Experiment VI) - Ring Size Separation in Chromegabond Diamine (see Conditions in Table 3 and Concentrations in Table 5A)

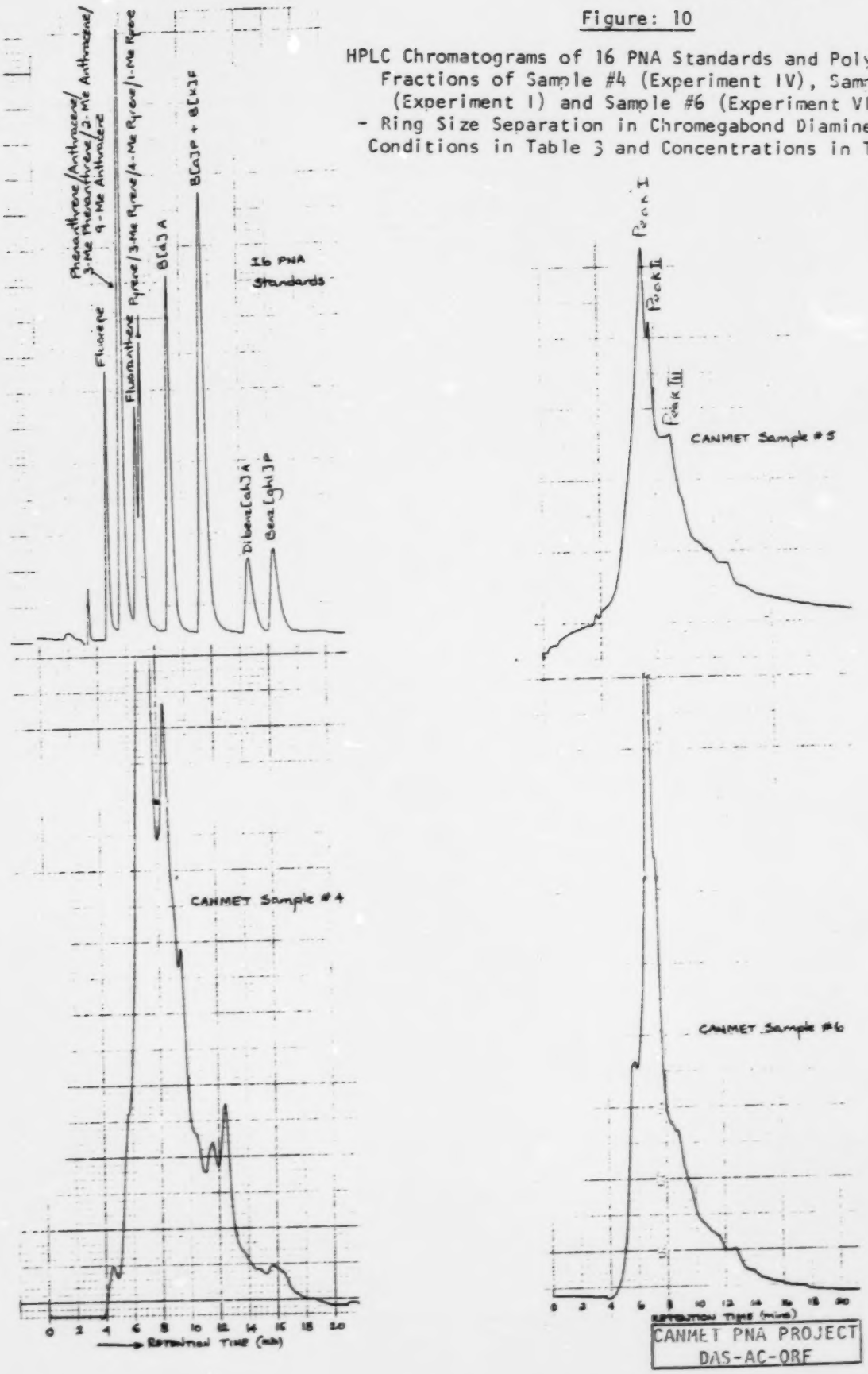


Figure: 10A

HPLC-UV Chromatogram of Major PNA Fractions Isolated from
Semipreparative Ring Size Separation of Sample #5 (Experiment I)
Polyaromatic Fraction on Chromegabond Diamine

Conditions: Isocratic, C_{18}RP Ultrasphere ODS (4.6 mm x 25 cm, 5 μm), 70% CH_3CN, 1.0 mL/min, UV @ 254 nm, 20 μL injection, SP 4100 Data System

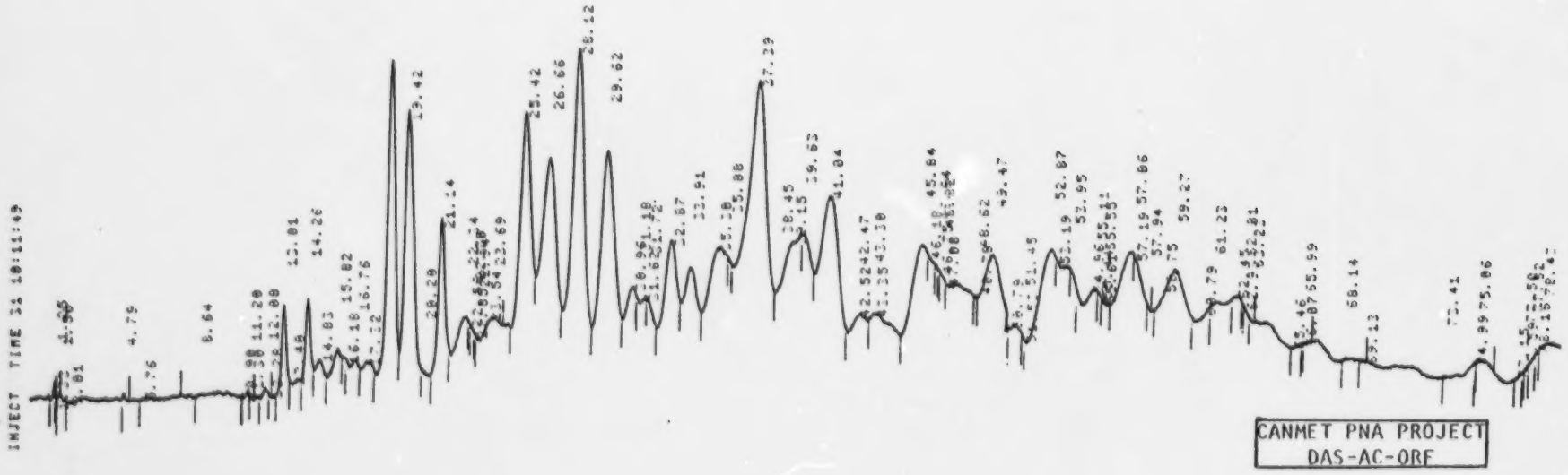


Figure: 11

HPLC Chromatograms of 10 PNA Standards and Polyaromatic Fractions of Sample #1 (Experiment X), Sample #2 (Experiment XIII) and Sample #3 (Experiment XII) - Ring Size Separation in μ Bondapak NH_2 (see Conditions in Table 3 and Concentrations in Table 6A)

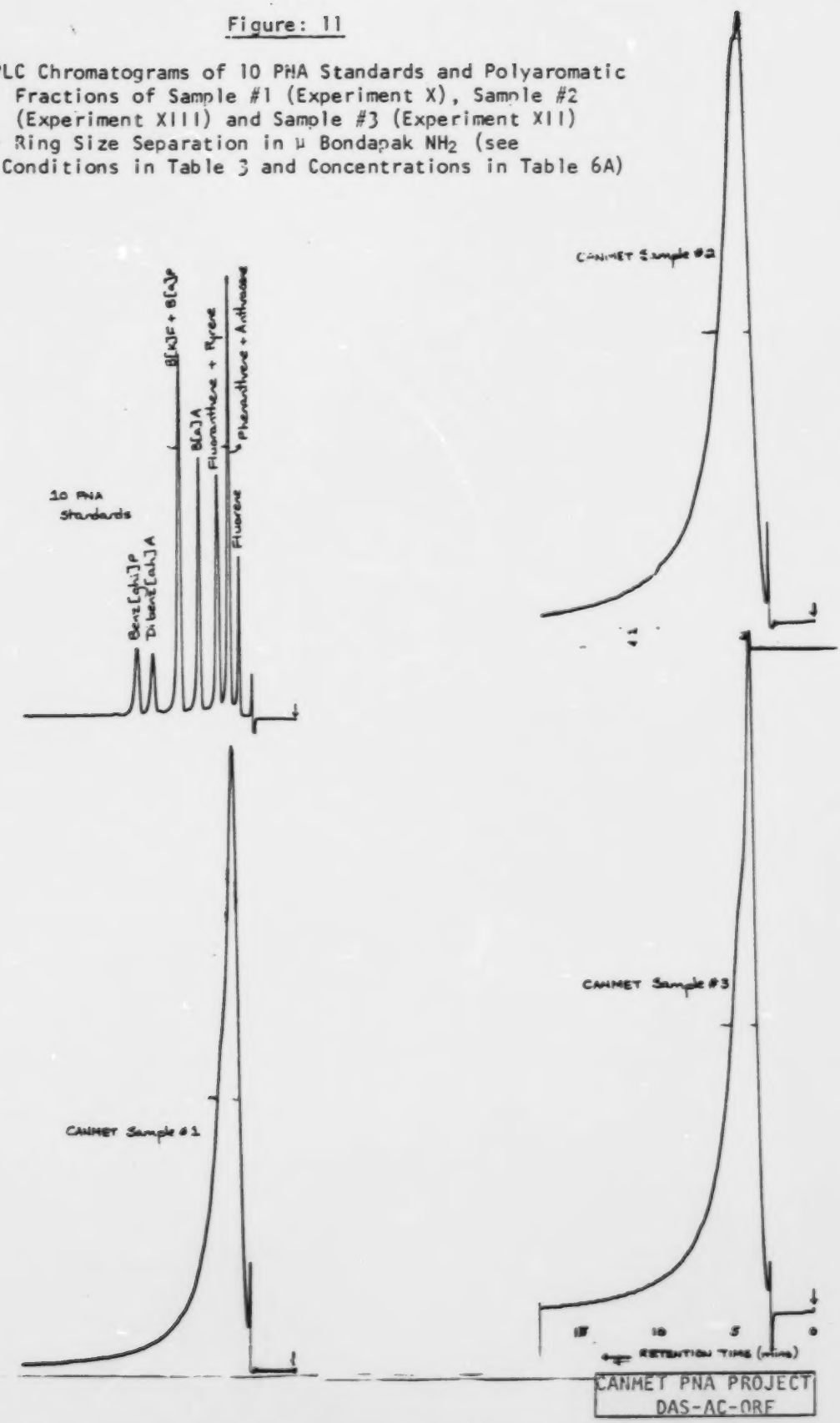
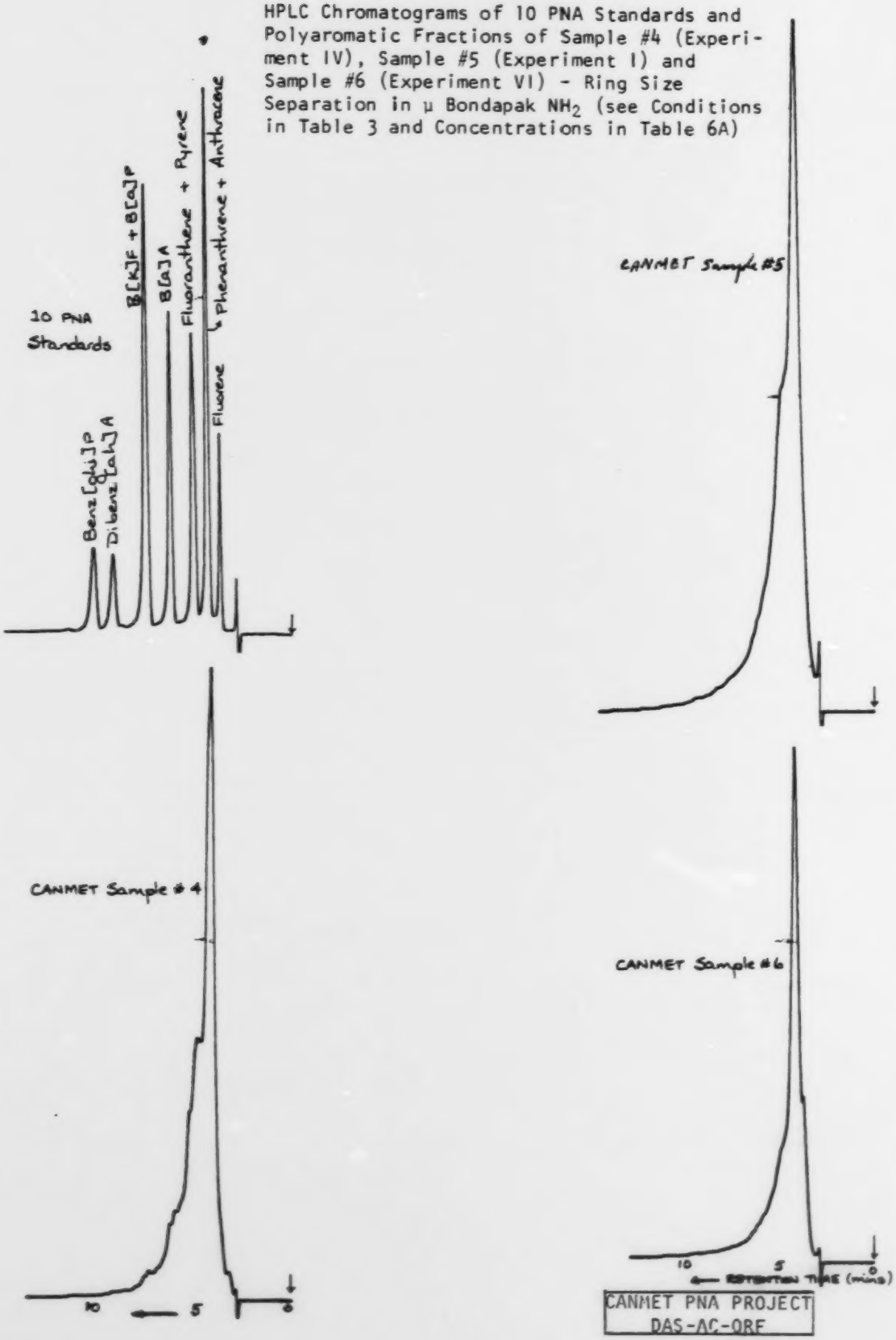


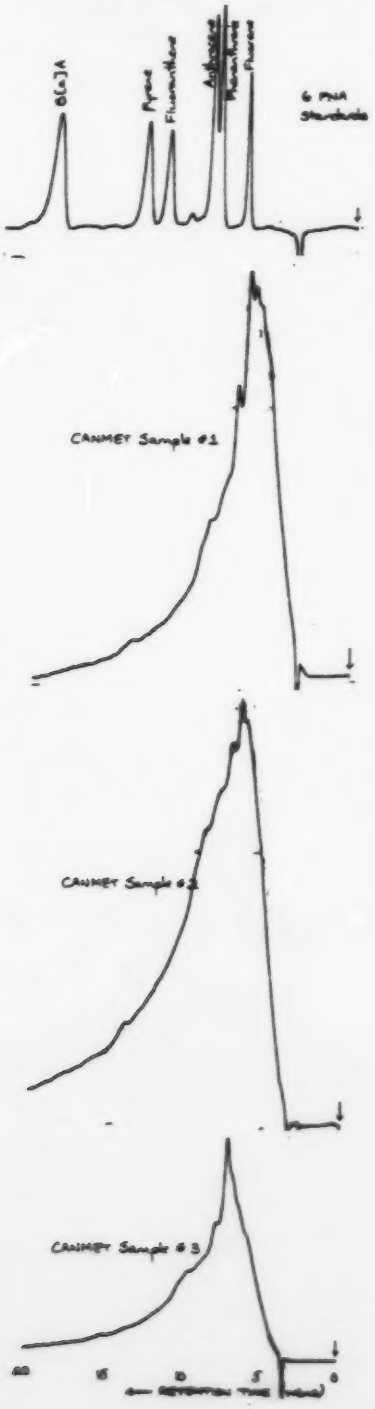
Figure: 12

HPLC Chromatograms of 10 PNA Standards and Polyaromatic Fractions of Sample #4 (Experiment IV), Sample #5 (Experiment I) and Sample #6 (Experiment VI) - Ring Size Separation in μ Bondapak NH_2 (see Conditions in Table 3 and Concentrations in Table 6A)



Figures: 13 & 14

HPLC Chromatograms of 6 PNA Standards and Polyaromatic Fractions of Sample #1 (Experiment X), Sample #2 (Experiment XIII), Sample #3 (Experiment XII) in Figure 13 and Same 6 PNA Standards and Polyaromatic Fractions of Sample #4 (Experiment IV), Sample #5 (Experiment #1), Sample #6 (Experiment VI) in Fig.14 - Ring Size Separation in Partisil PAC (cyanoamine)(see Conditions in Table 3 and Concentrations in Table 6A)



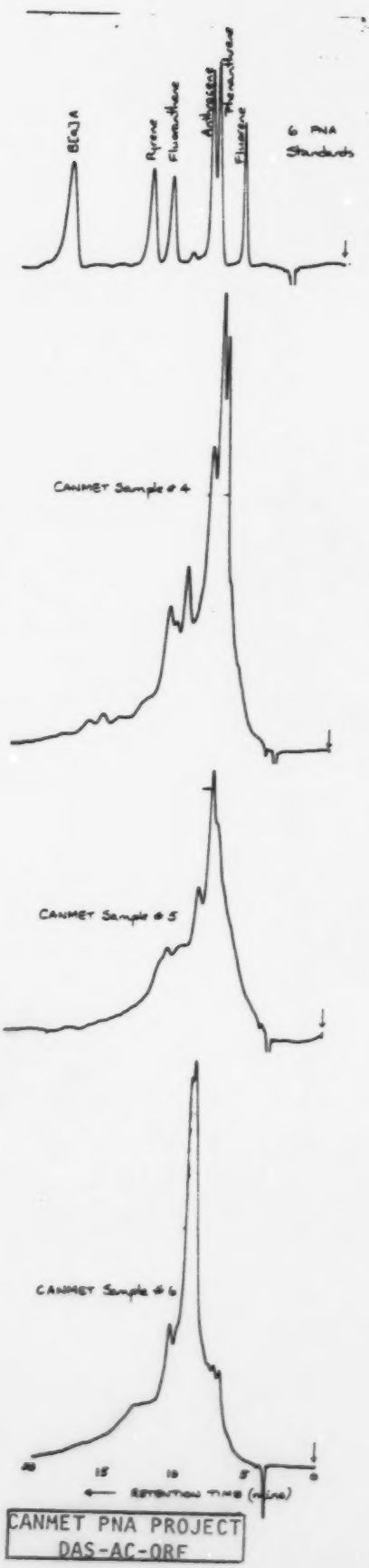


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Figure: 15

Size Exclusion Chromatograms of 10 PNA Standards and Polyaromatic Fractions of Sample #1 (Experiment IX), Sample #2 (Experiment XIV), Sample #3 (Experiment XI), Sample #4 (Experiment V), Sample #5 (Experiment III) and Sample #6 (Experiment VII) - Molecular Size Separations in μ-Styragel (100Å) in Series with μ-Spherogel (50Å) (see Conditions in Table 4 and Concentations in Table 6A)

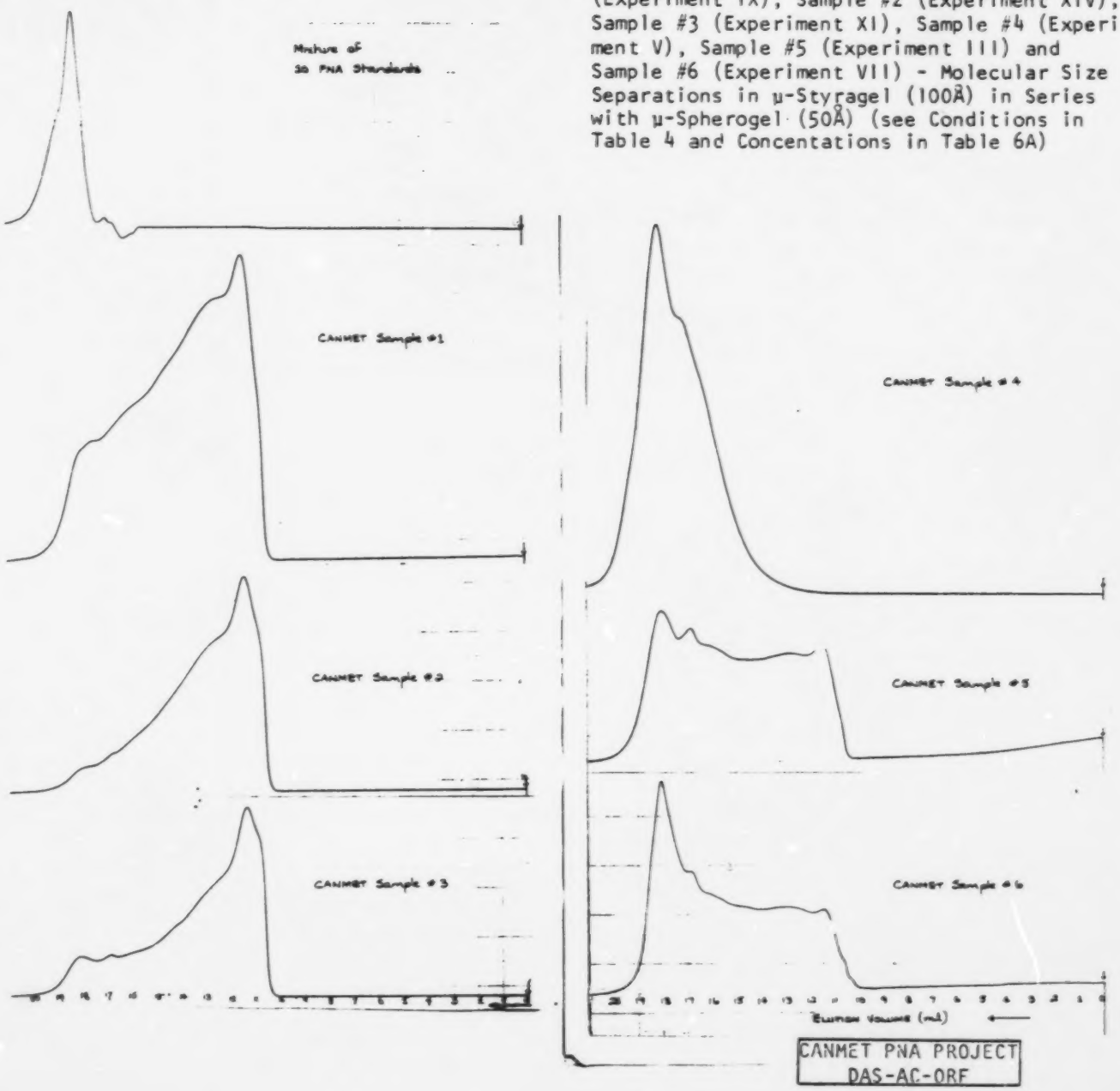


Figure 16 : HPLC-Fluorescence Chromatogram of 24 PNA Standards

(Conditions in Table 5)
(& Concentrations in Table 6A)

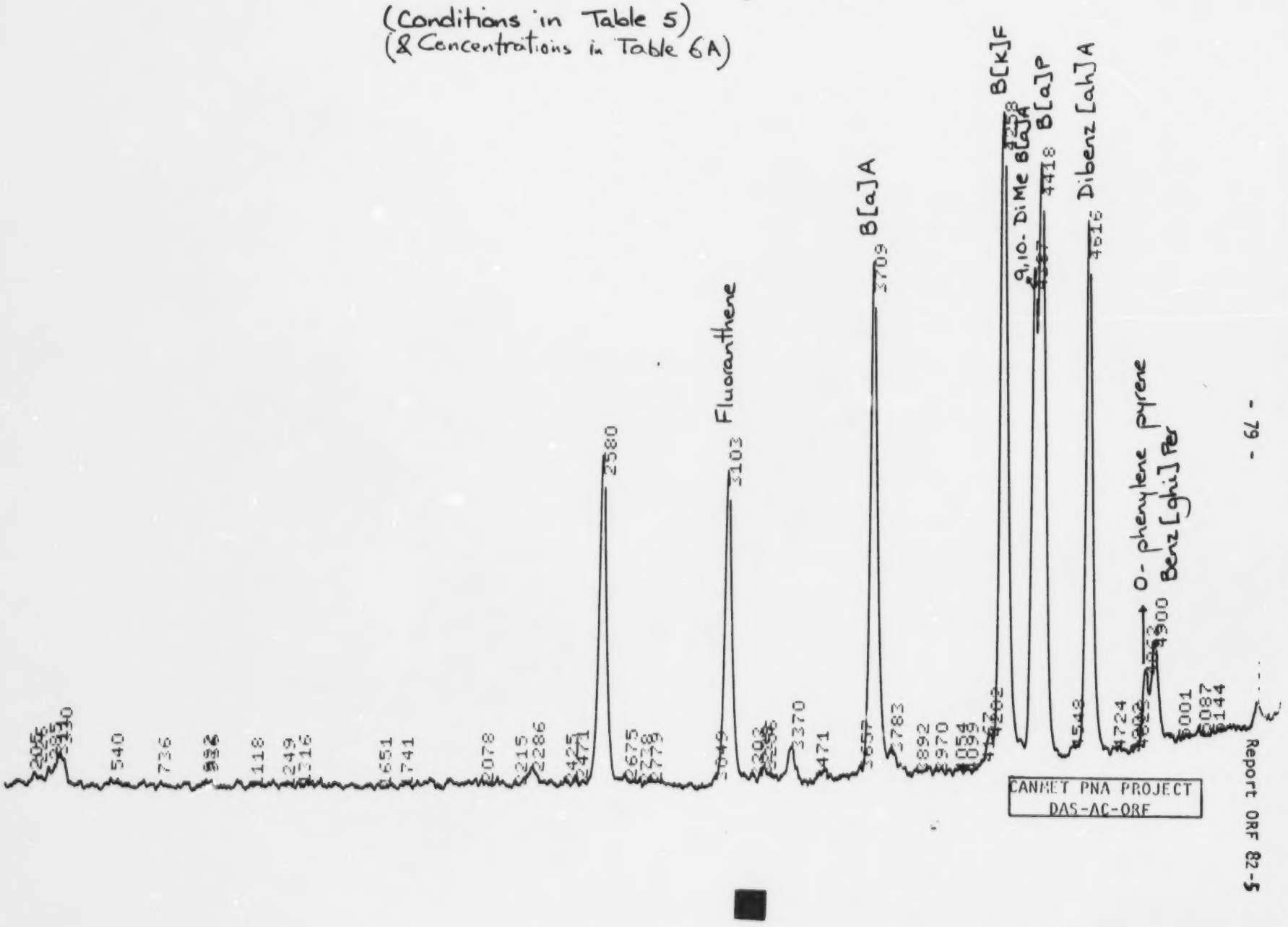
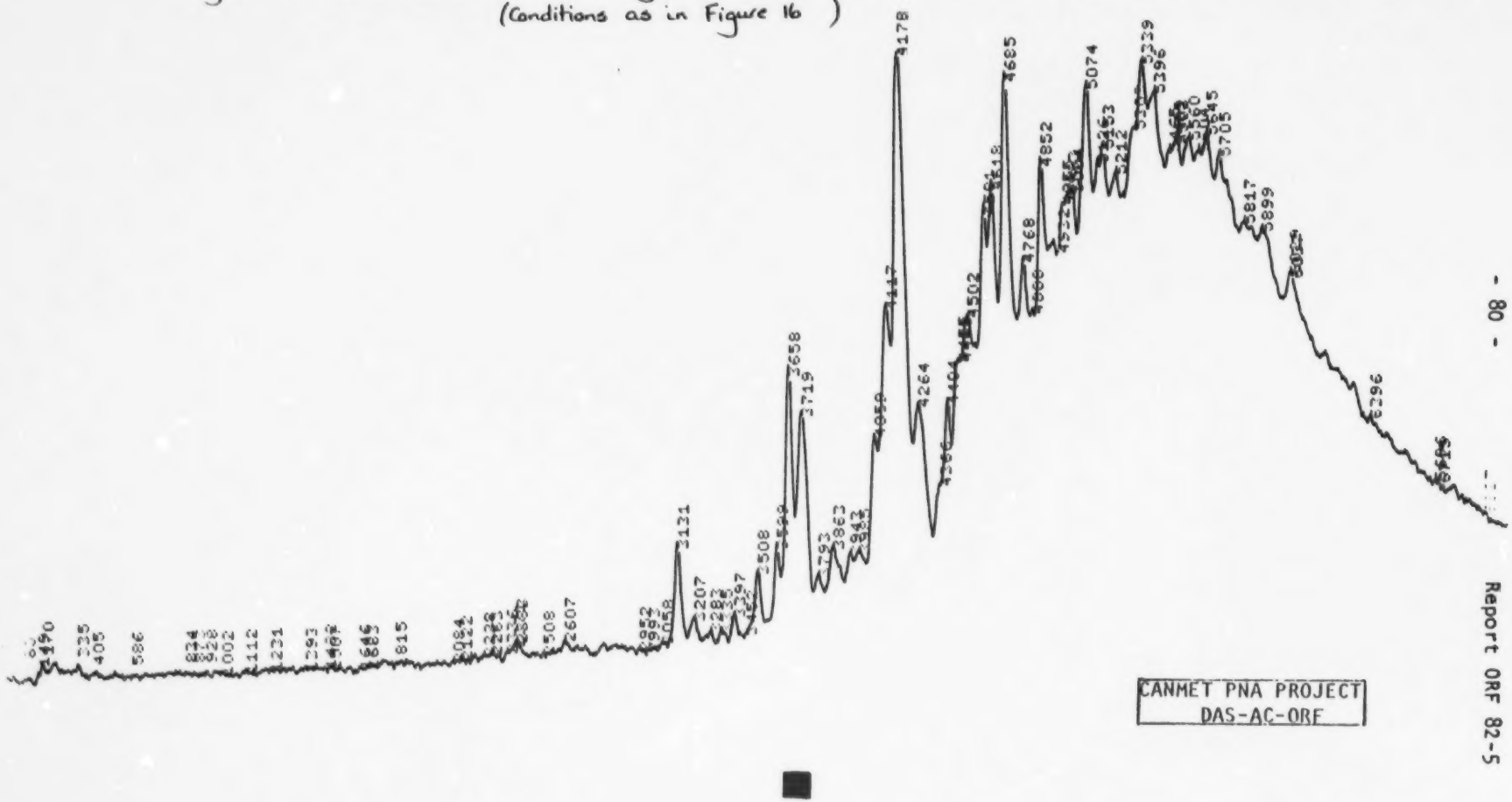


Figure 17 : HPLC-Fluorescence Chromatogram of CANMET Sample No. 1 Acid-Base cleaned Polyaromatic Fraction (Expt. X)
(Conditions as in Figure 16)



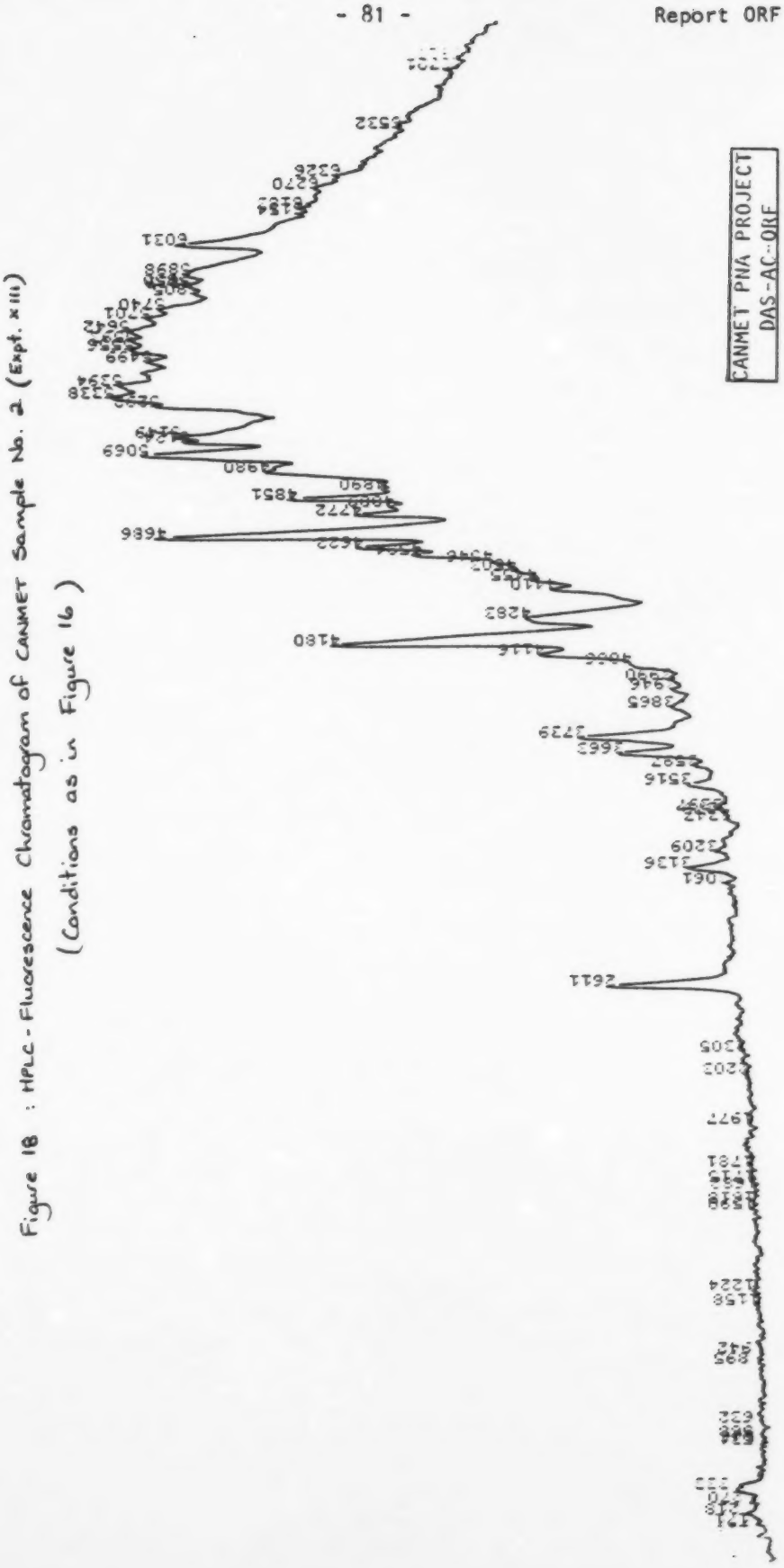


Figure 18 : HPLC - Fluorescence Chromatogram of CANMET Sample No. 2 (Expt. x111)
(Conditions as in Figure 16)

Figure 19 : HPLC - Fluorescence Chromatogram of CANMET Sample No. 3 (Expt. X11)
(Conditions as in Figure 16)

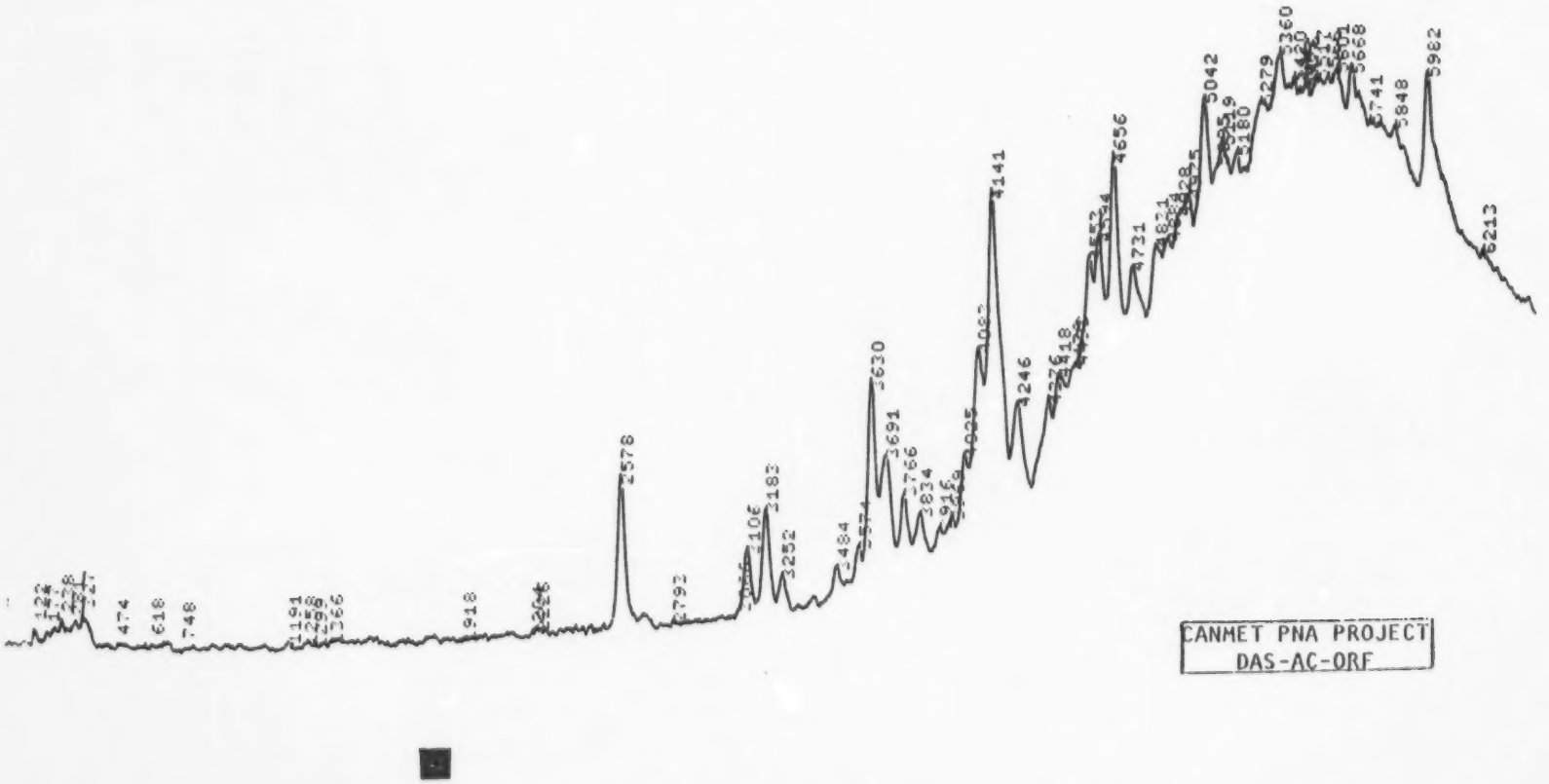


Figure 20 : HPLC - Fluorescence Chromatogram of CANMET Sample No. 4 (Expt IV)
(Conditions as in Figure 16)

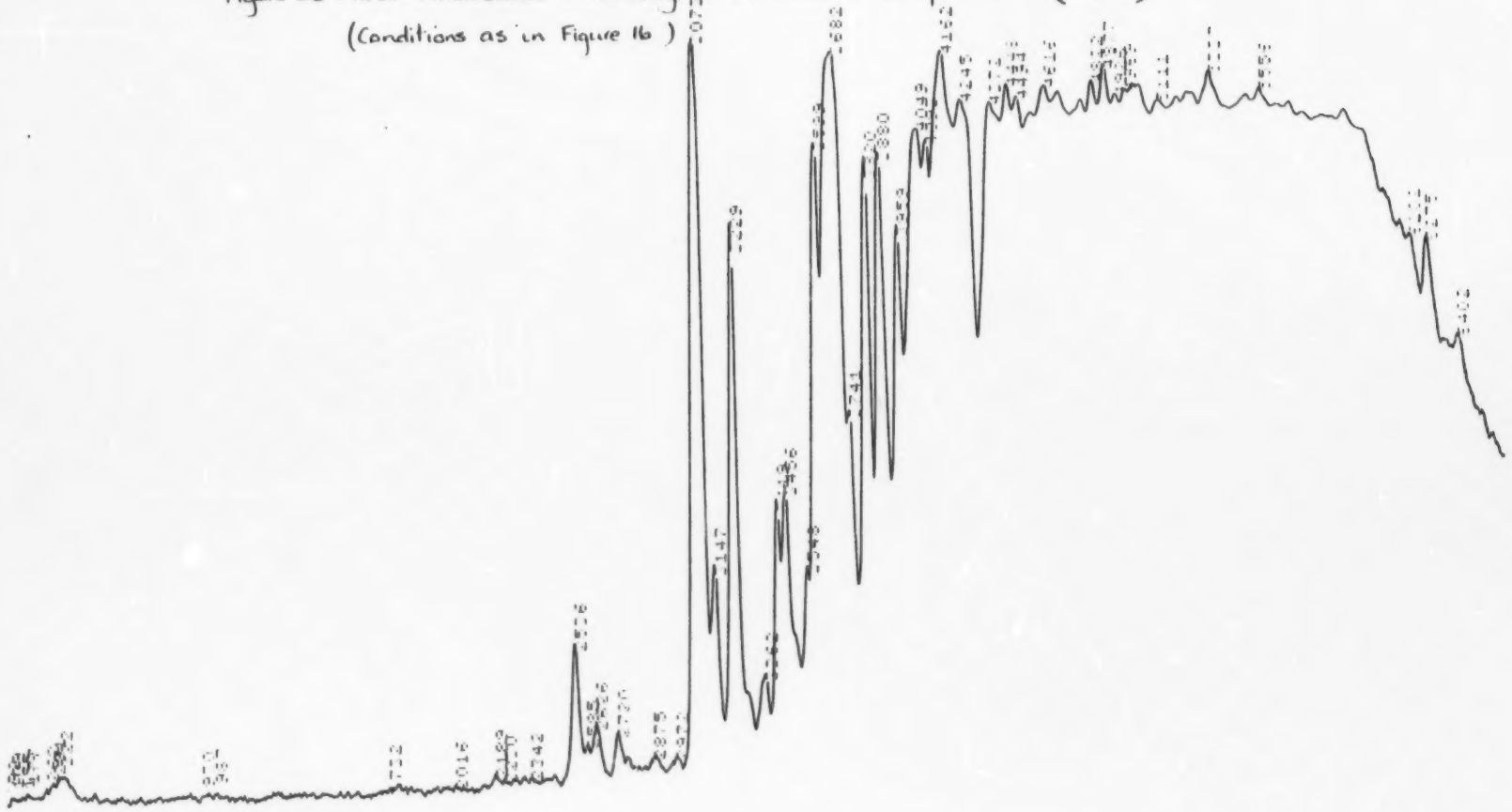


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Figure 21 : HPLC - Fluorescence Chromatogram of CANMET Sample No. 5 (Expt 1)

(Conditions as in Figure 16)

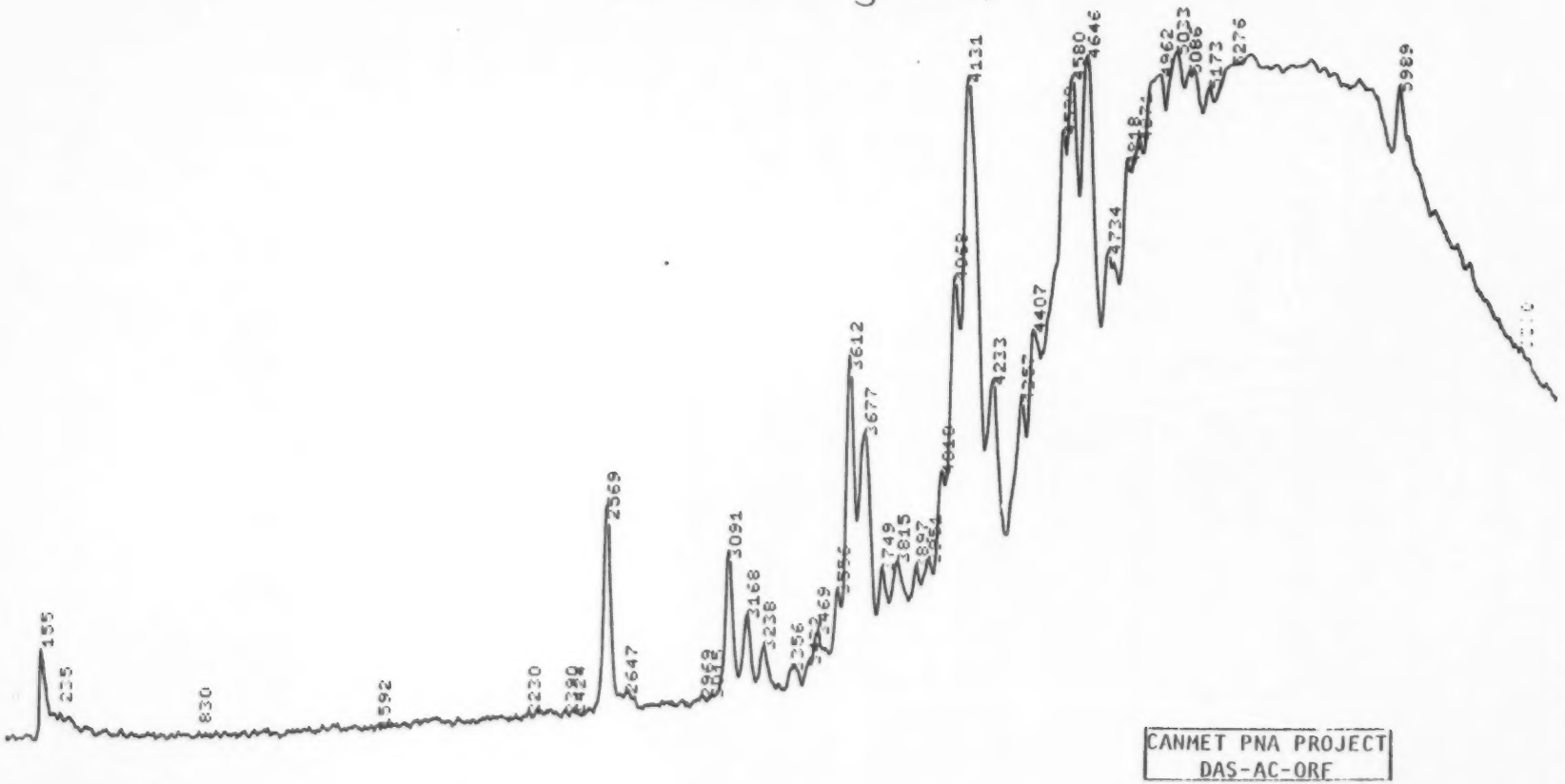

Figure 22 : HPLC- Fluorescence Chromatogram of CANMET Sample No. 6 (Expt: VI)
(Conditions as in Figure 16)

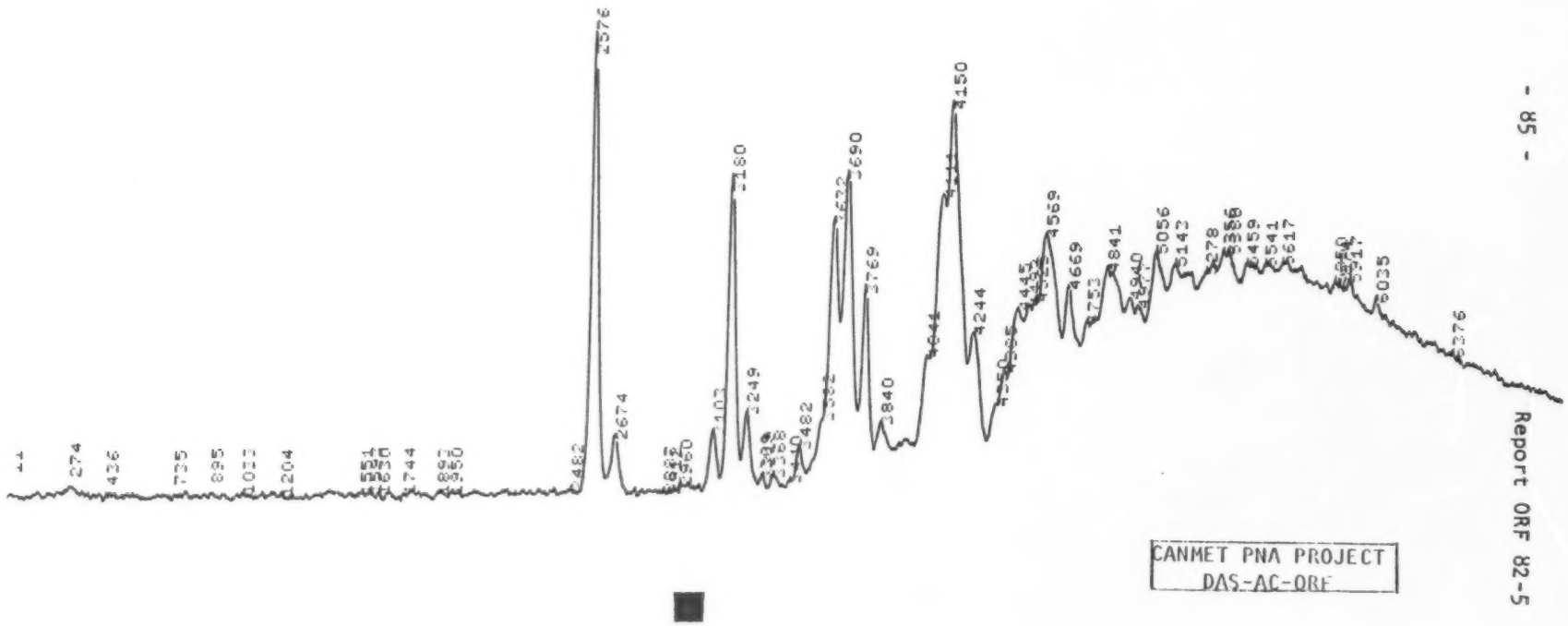

Figure 23 : HPLC-UV Chromatogram of 24 PNA Standards
(Conditions in Table 5)
& Concentrations in Table 6A)

Figure 24 : HPLC-UV Chromatogram of CANMET Sample No. 1 Acid-Base cleaned Polyaromatic Fraction (Expt X)
(Conditions as in Figure 23)

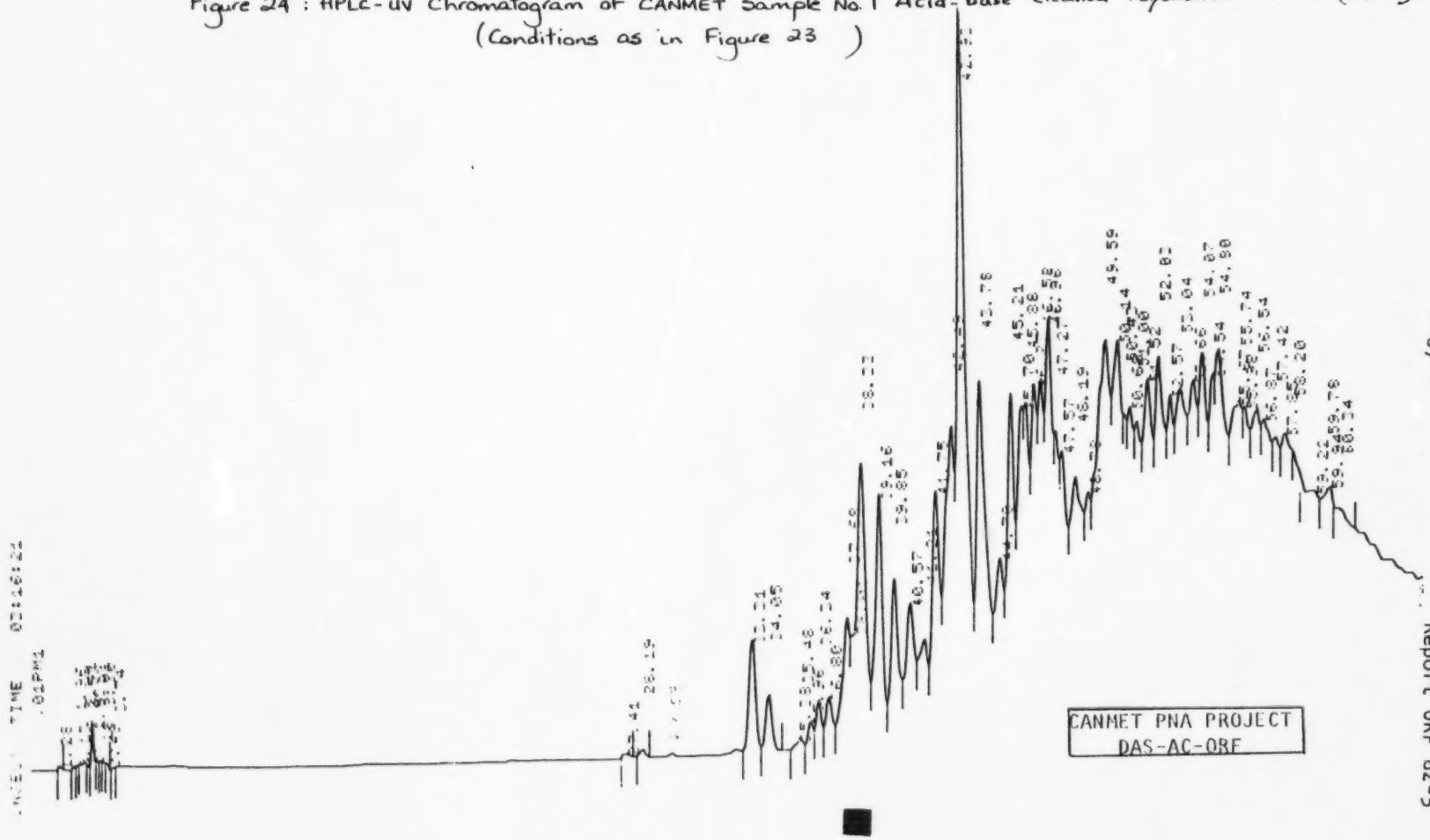

Figure 25 : HPLC-UV Chromatogram of CANMET Sample No. 2 (Expt. XIII)
(Conditions as in Figure 23)

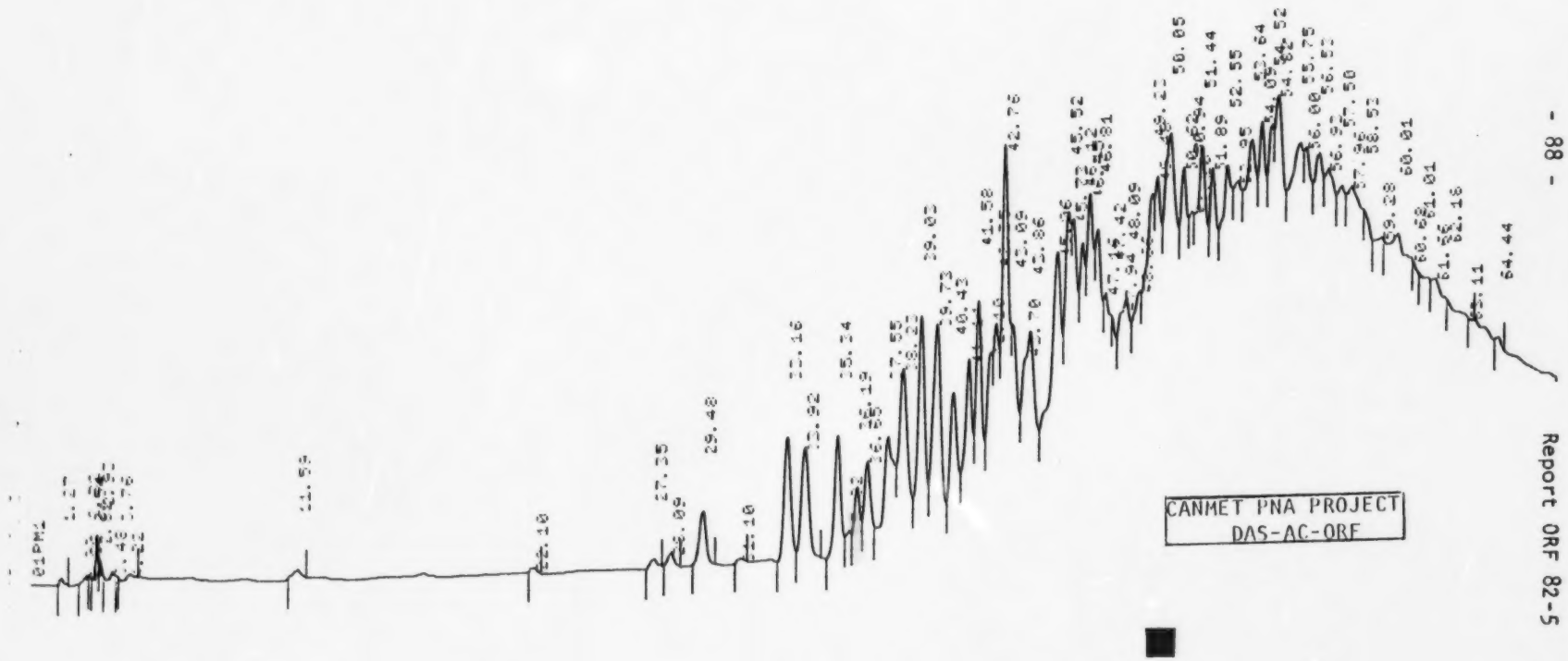

Figure 26: HPLC-UV Chromatogram of CANMET Sample No. 3 (Expt. XII)

(Conditions as in Figure 23)

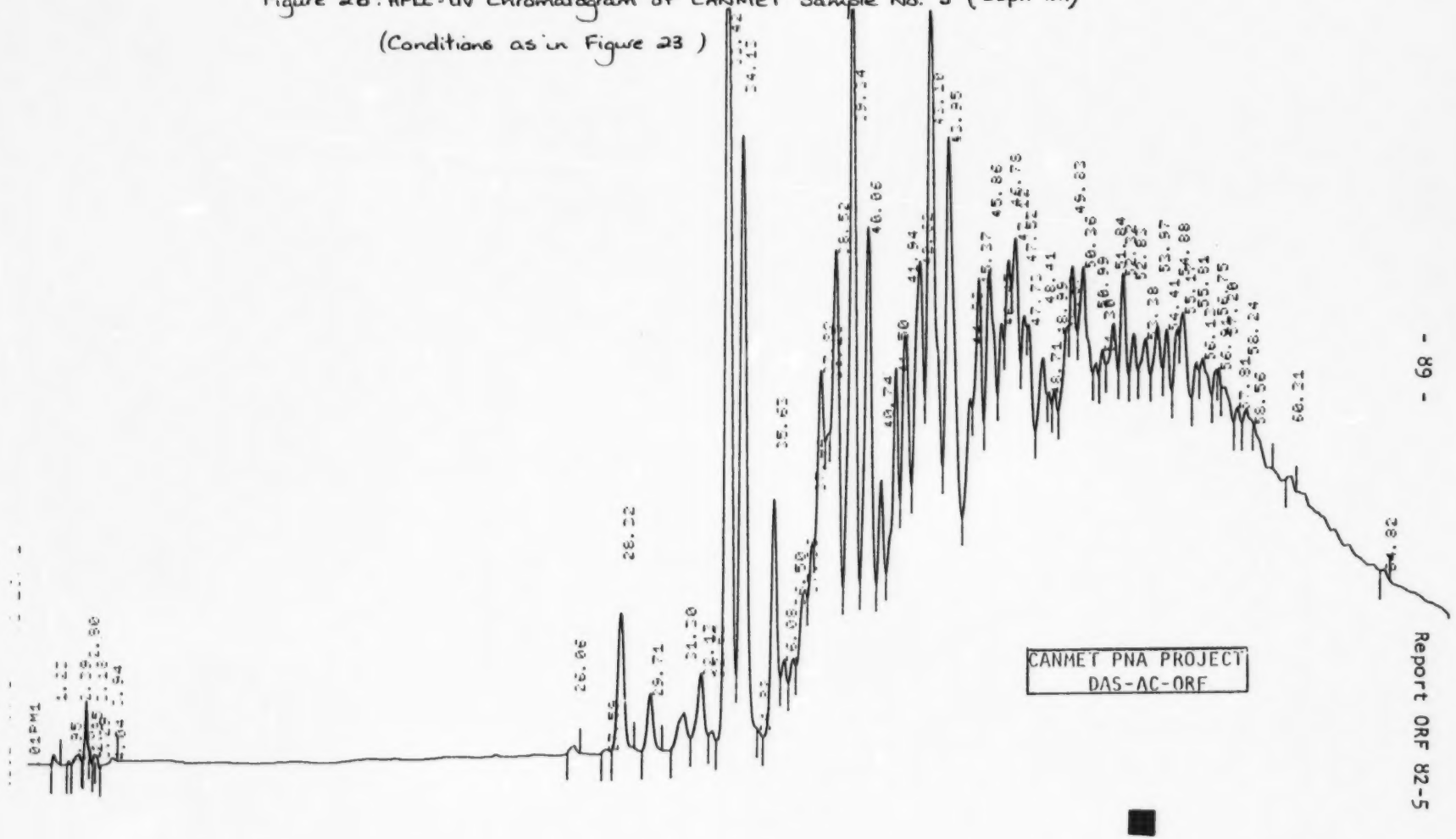

Figure 27 : HPLC-UV Chromatogram of CANMET Sample No. 4 (Expt. IV)

(Conditions as in Figure 23)

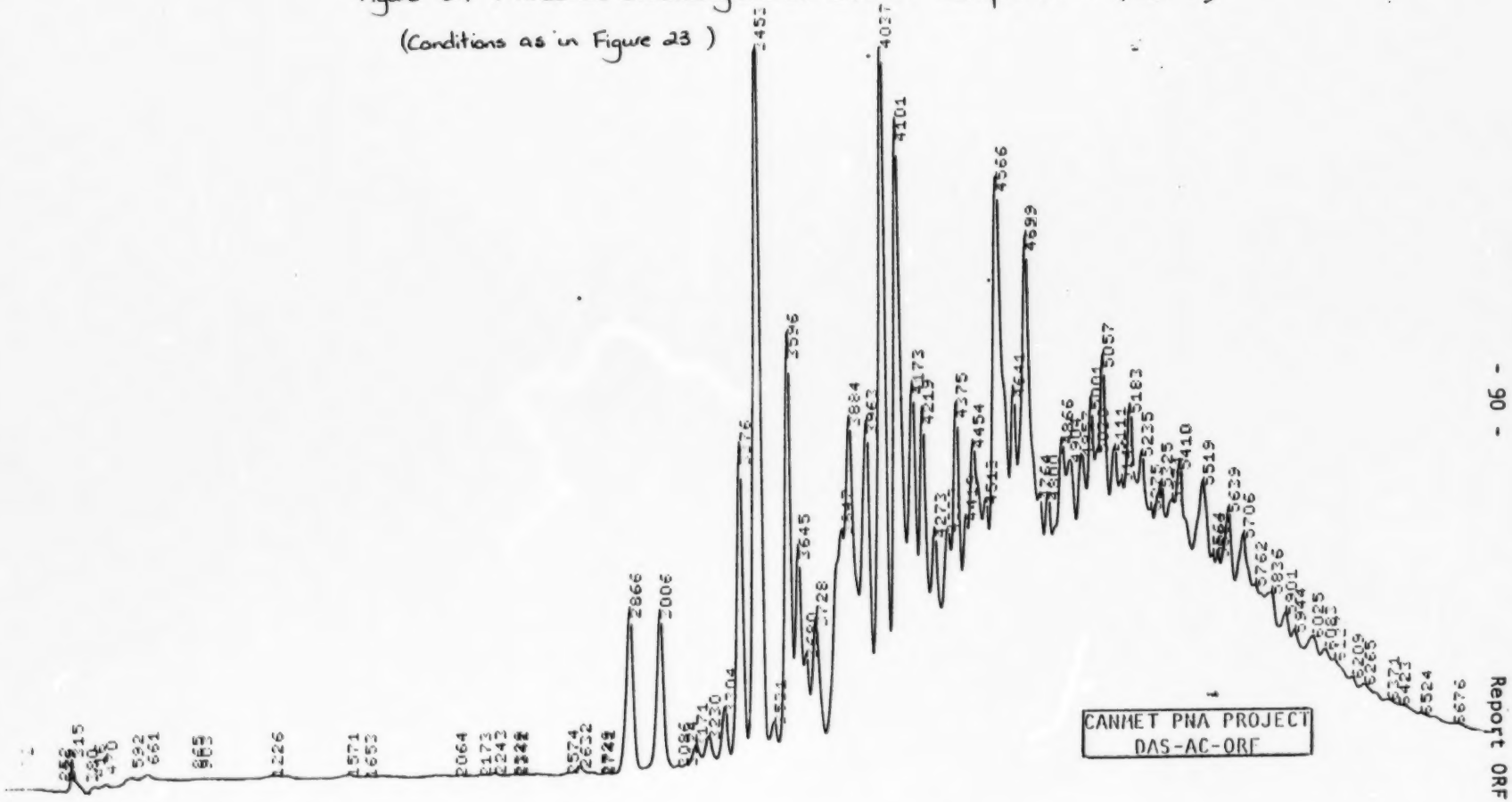

Figure 28 : HPLC-UV Chromatogram of CANMET Sample No. 5 (Expt. 1)
(Conditions as in Figure 23)

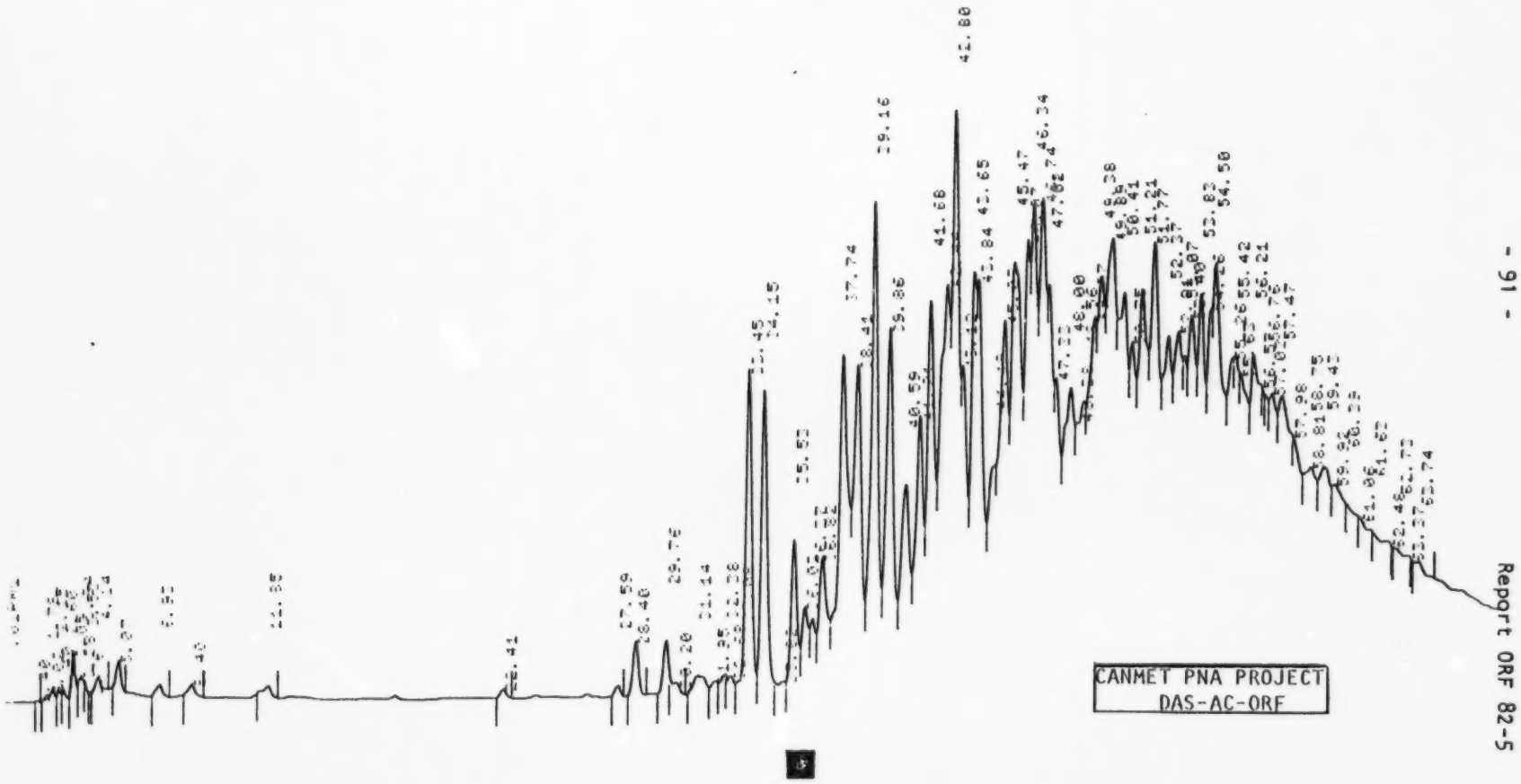

Figure 29 : HPLC-UV Chromatogram of CANMET Sample No. 6 (Expt V1)
(Conditions as in Figure 23)

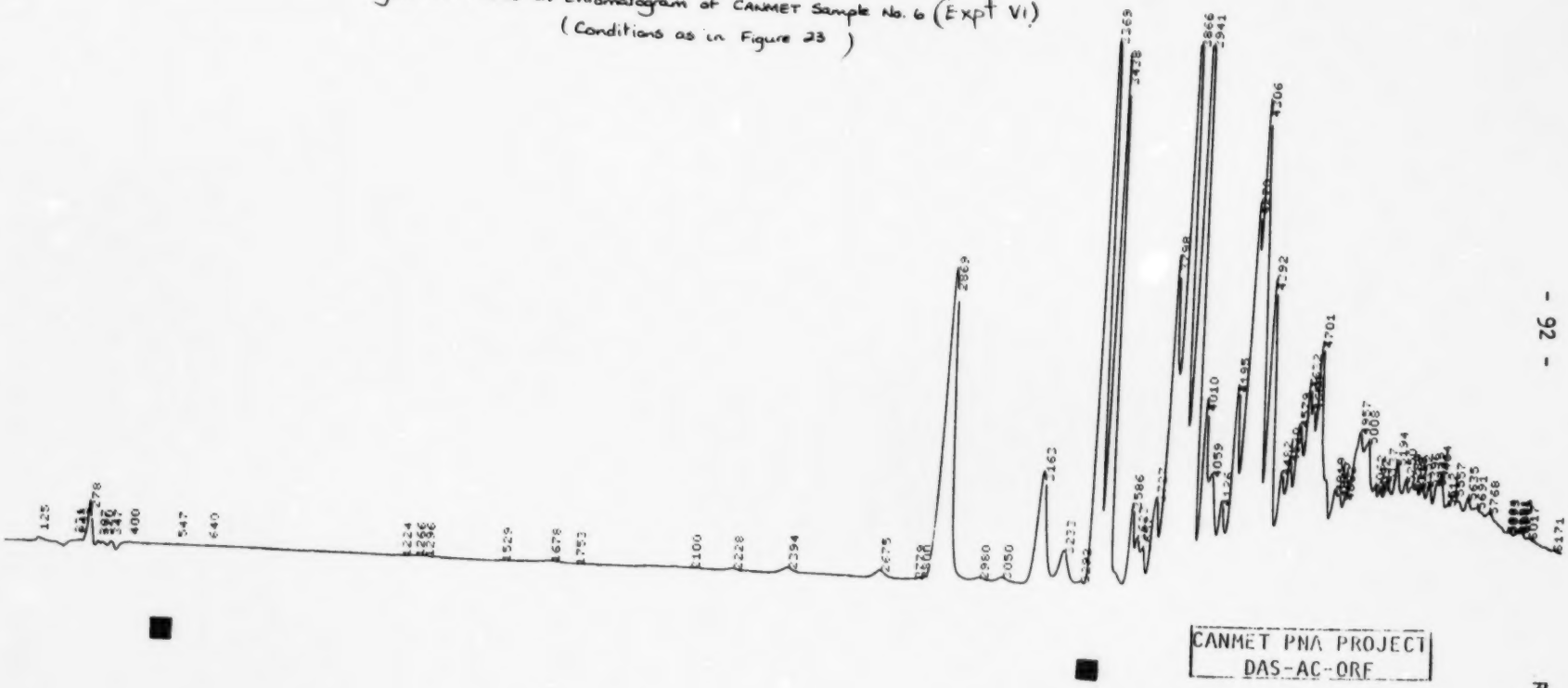

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Figure 30 : Capillary GC-FID Chromatogram of 24 PNA Standards
(Conditions in Table 6)
(Concentrations in Table 6A)

Figure 31 : Capillary GC-FID Chromatogram of CANMET Sample No. 1 (Expt x)
(Conditions as in Figure 30)

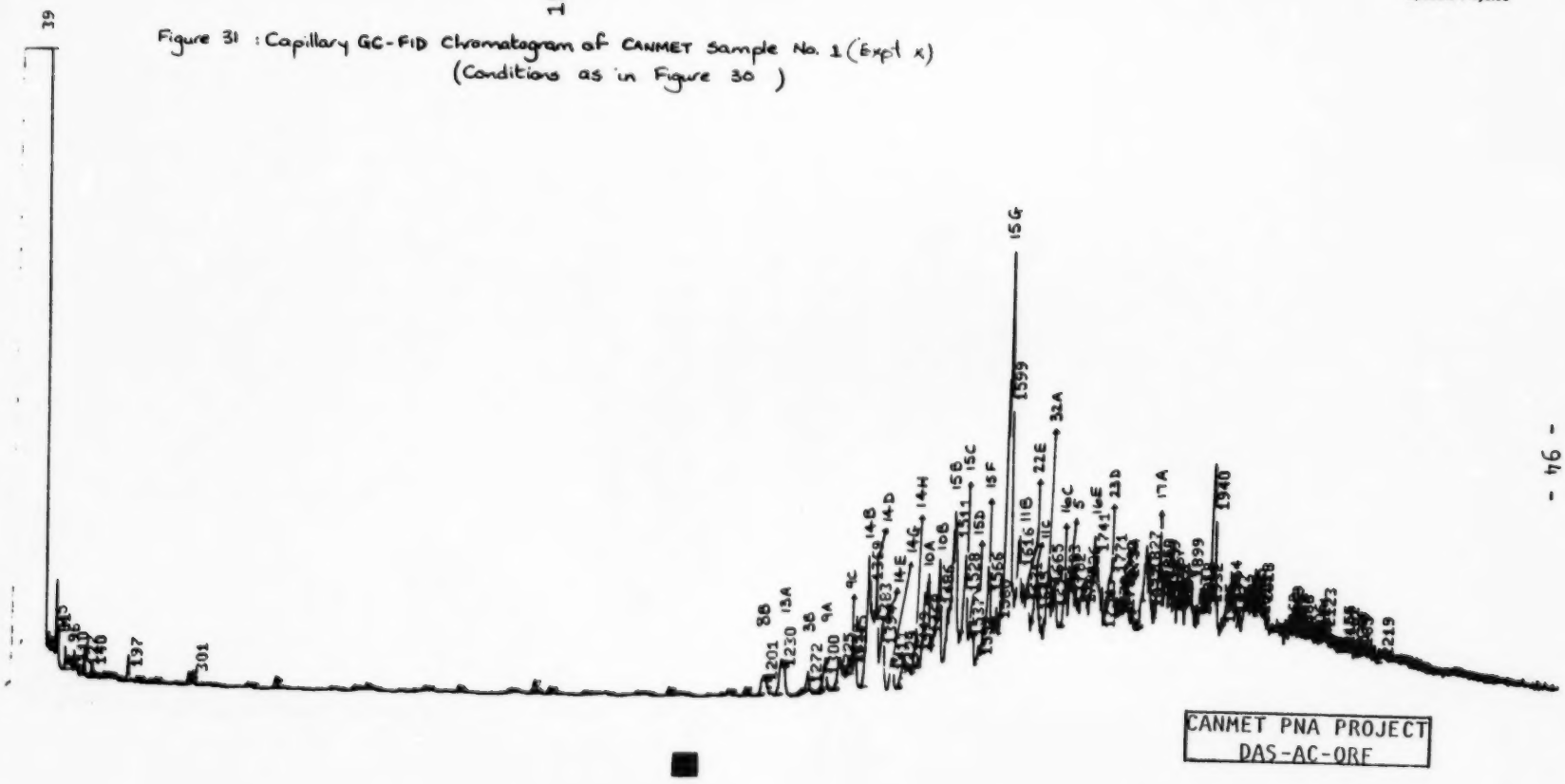


Figure 32 : Capillary Gc-FID Chromatogram of CANMET Sample No. 2 (Expt. XIII)
(Conditions as in Figure 30)

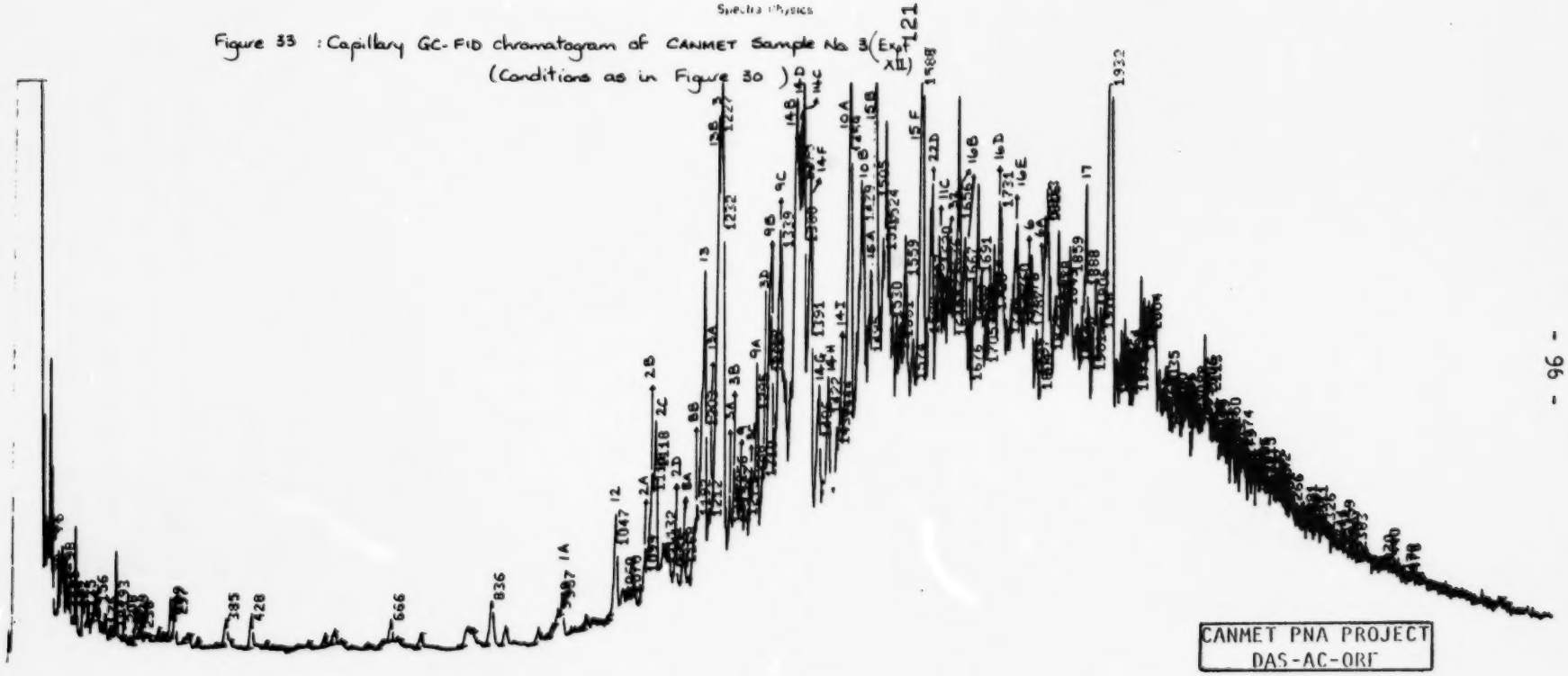
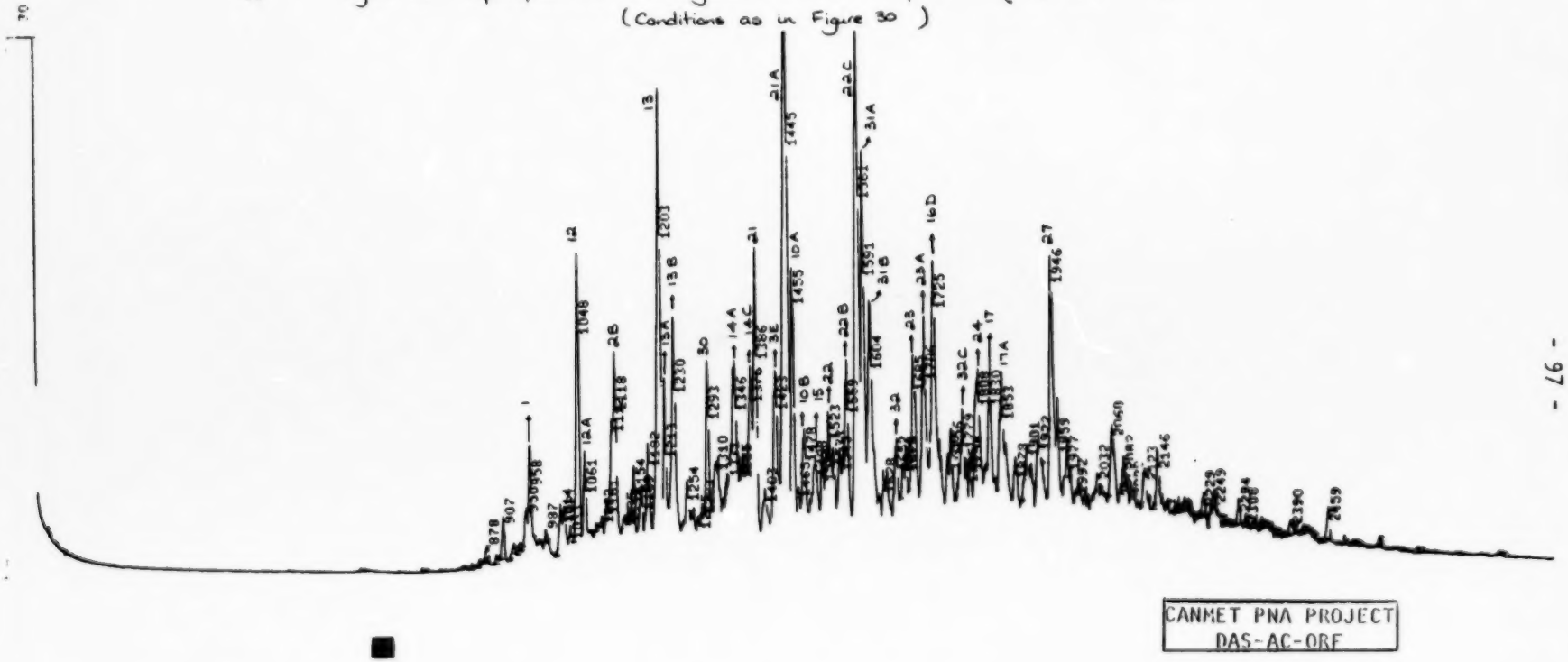


Figure 33 : Capillary GC-FID chromatogram of CANMET Sample No 3 (Exp. XII) (Conditions as in Figure 30)

Figure 34 : Capillary GC-FID Chromatogram of CANMET Sample No. 4 (Expt IV)
(Conditions as in Figure 30)



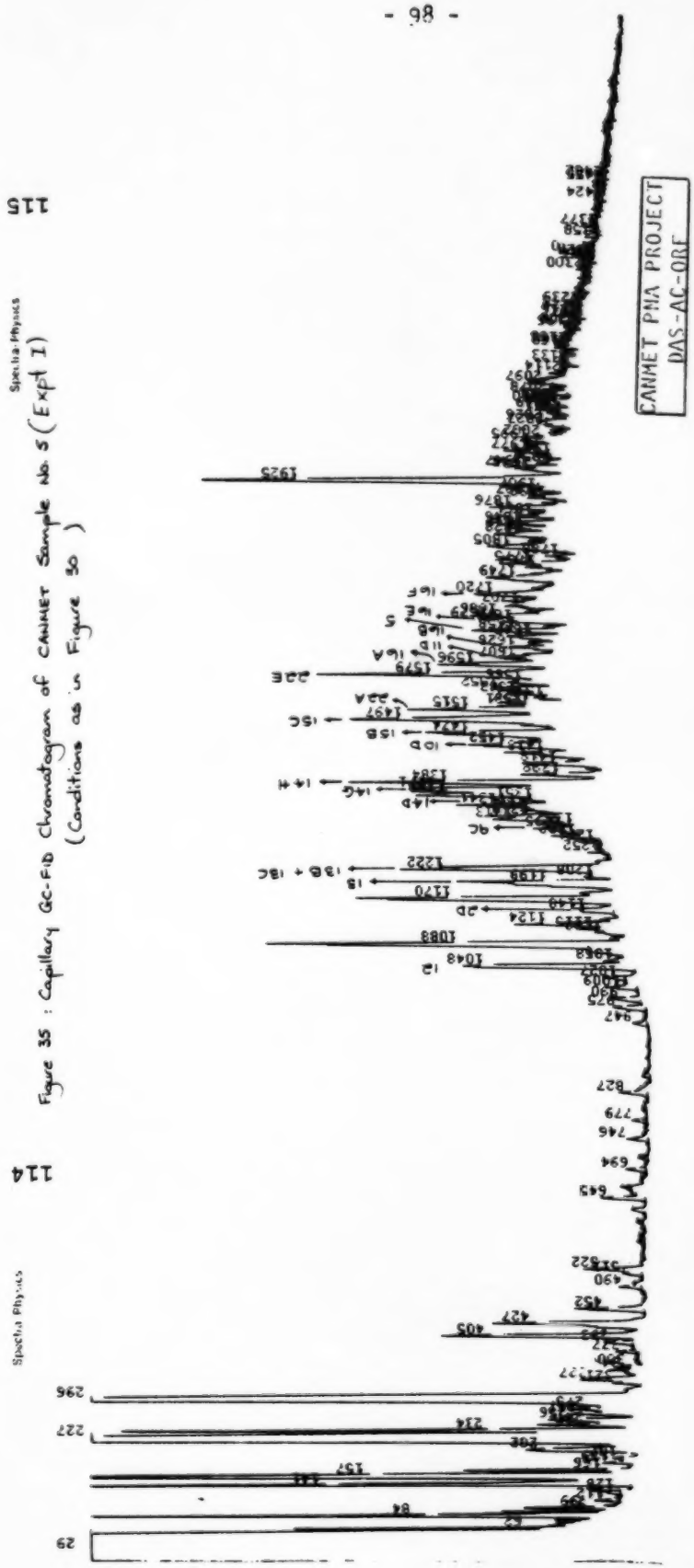
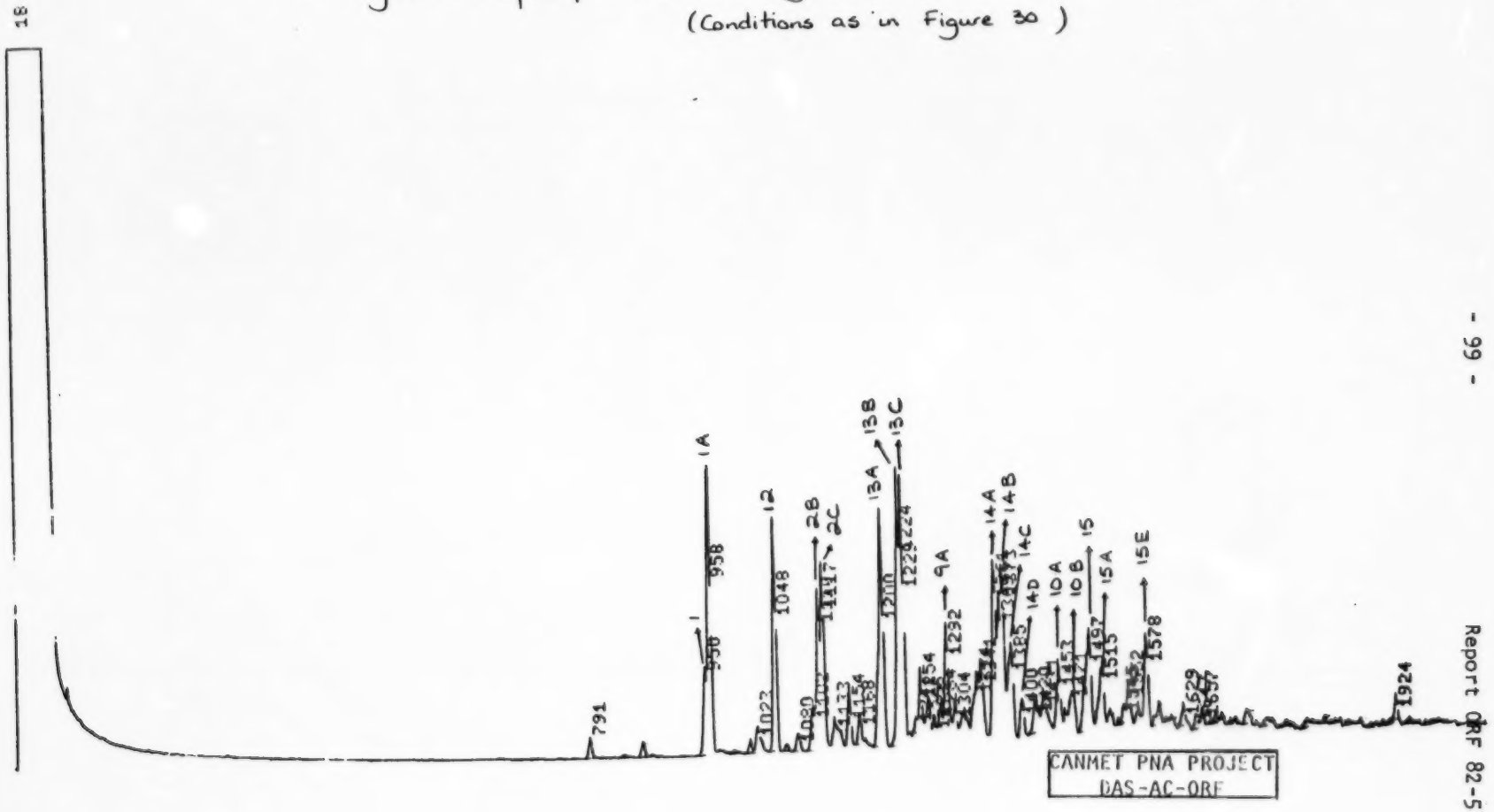


Figure 35 : Capillary GC-FID Chromatogram of CANMET Sample No. 5 (Expt I)
(Conditions as in Figure 30)

Figure 36 : Capillary GC-FID Chromatogram of CANMET Sample No. 6 (Expt. VI)
(Conditions as in Figure 30)



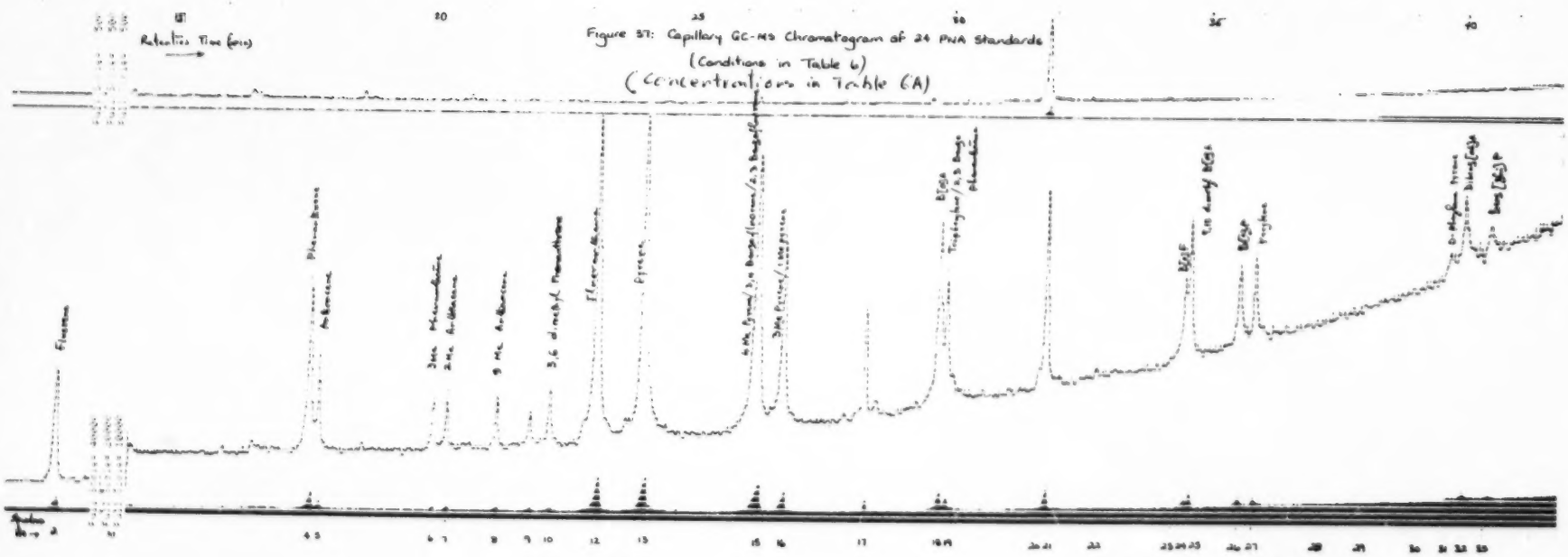


Figure 37: Capillary GC-MS Chromatogram of 24 PNA Standards
(Conditions in Table 6)
(Concentrations in Table 6A)

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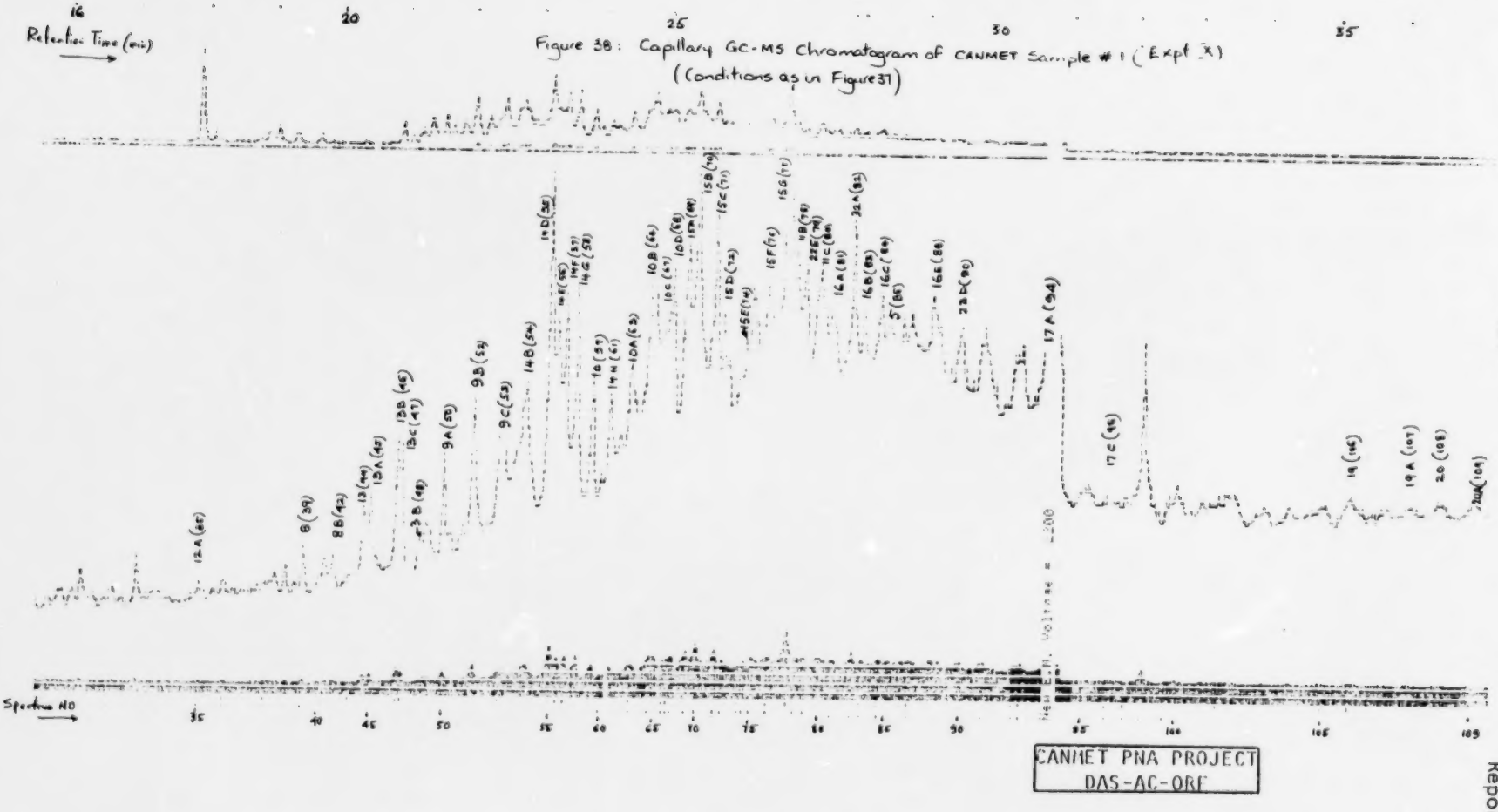

Figure 38: Capillary GC-MS Chromatogram of CANMET Sample # 1 (Expt X)
(Conditions as in Figure 31)

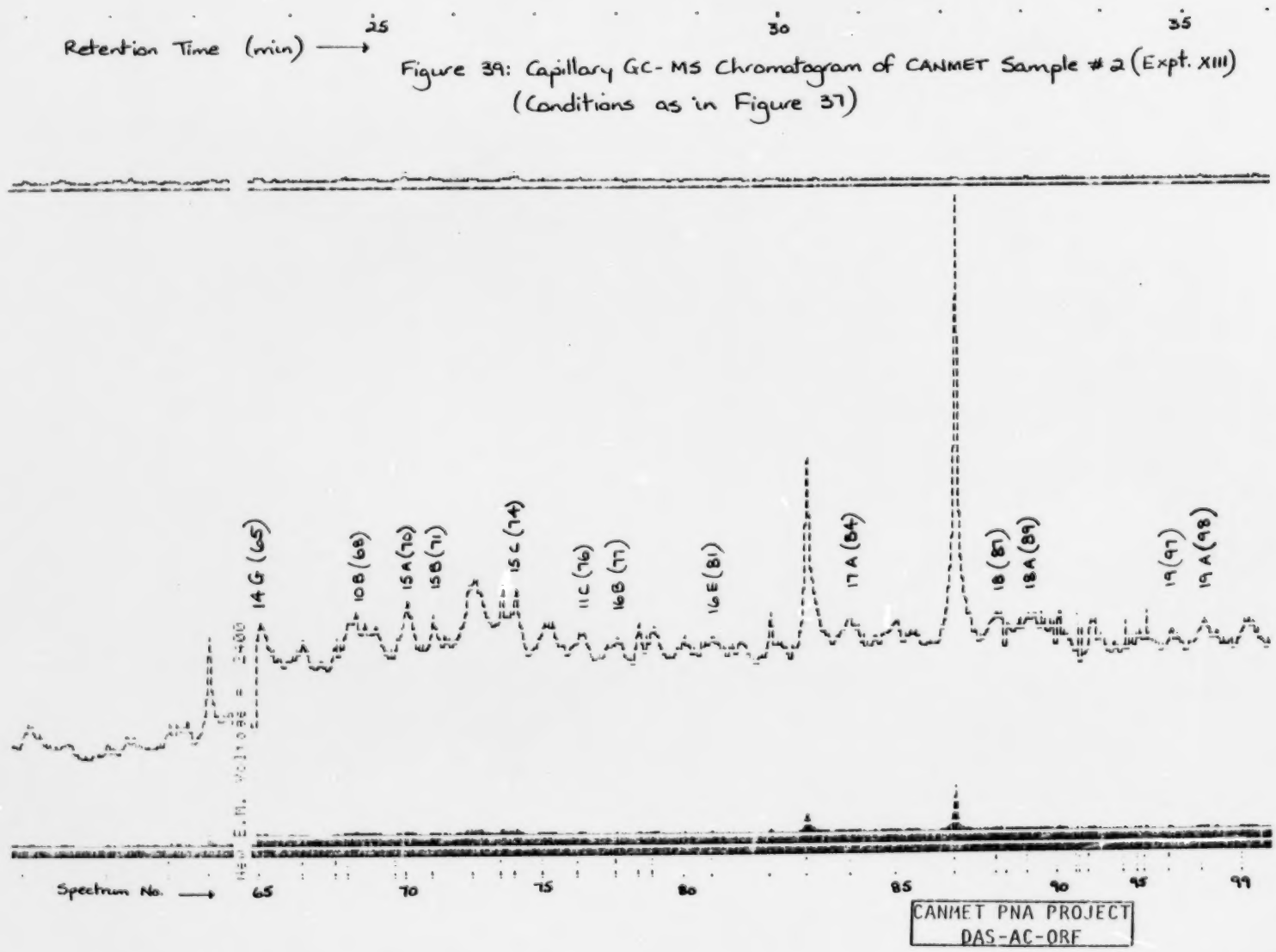

Figure 39: Capillary GC-MS Chromatogram of CANMET Sample # 2 (Expt. XIII)
(Conditions as in Figure 37)

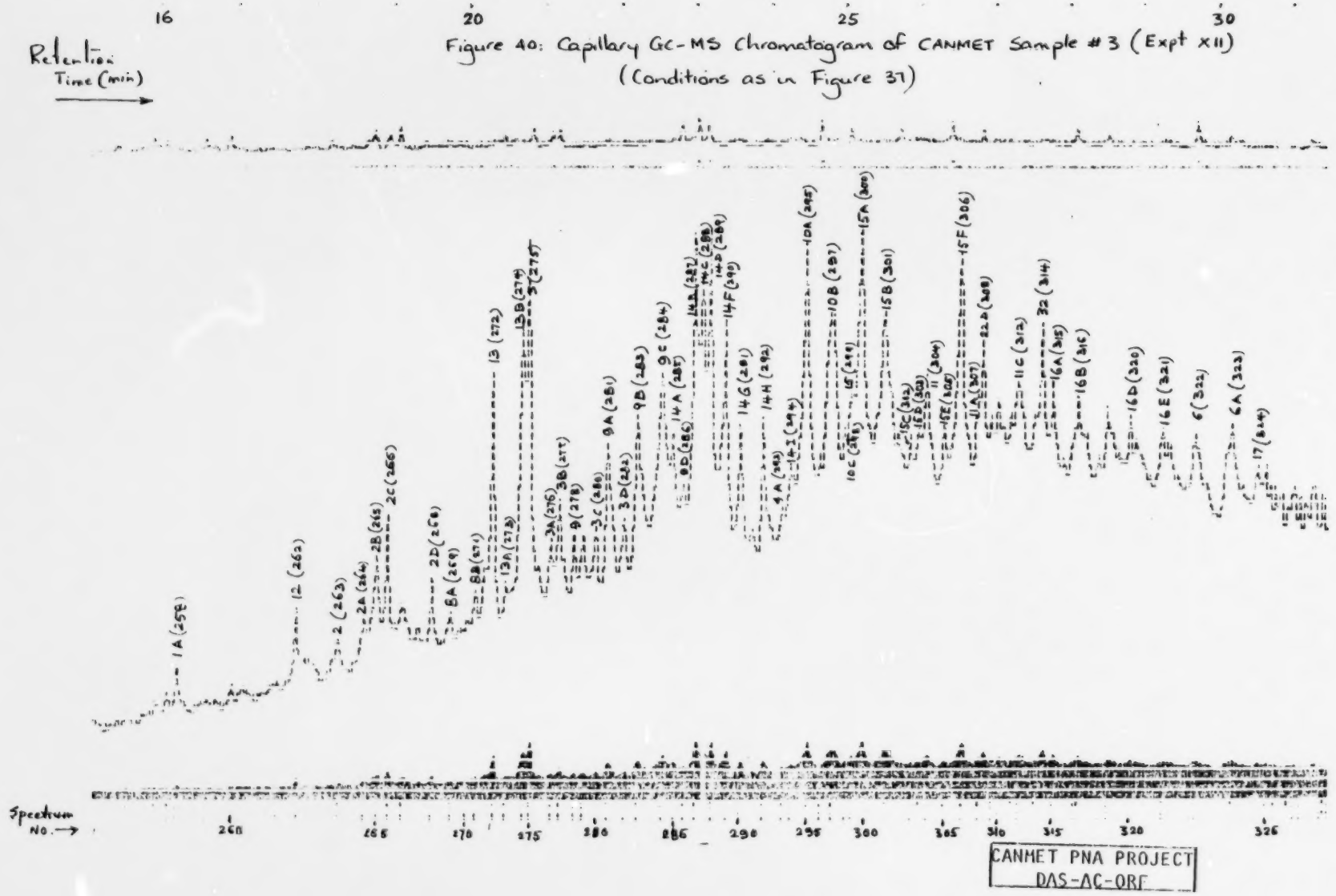

Figure 40: Capillary GC-MS Chromatogram of CANMET Sample #3 (Expt XII)
(Conditions as in Figure 37)

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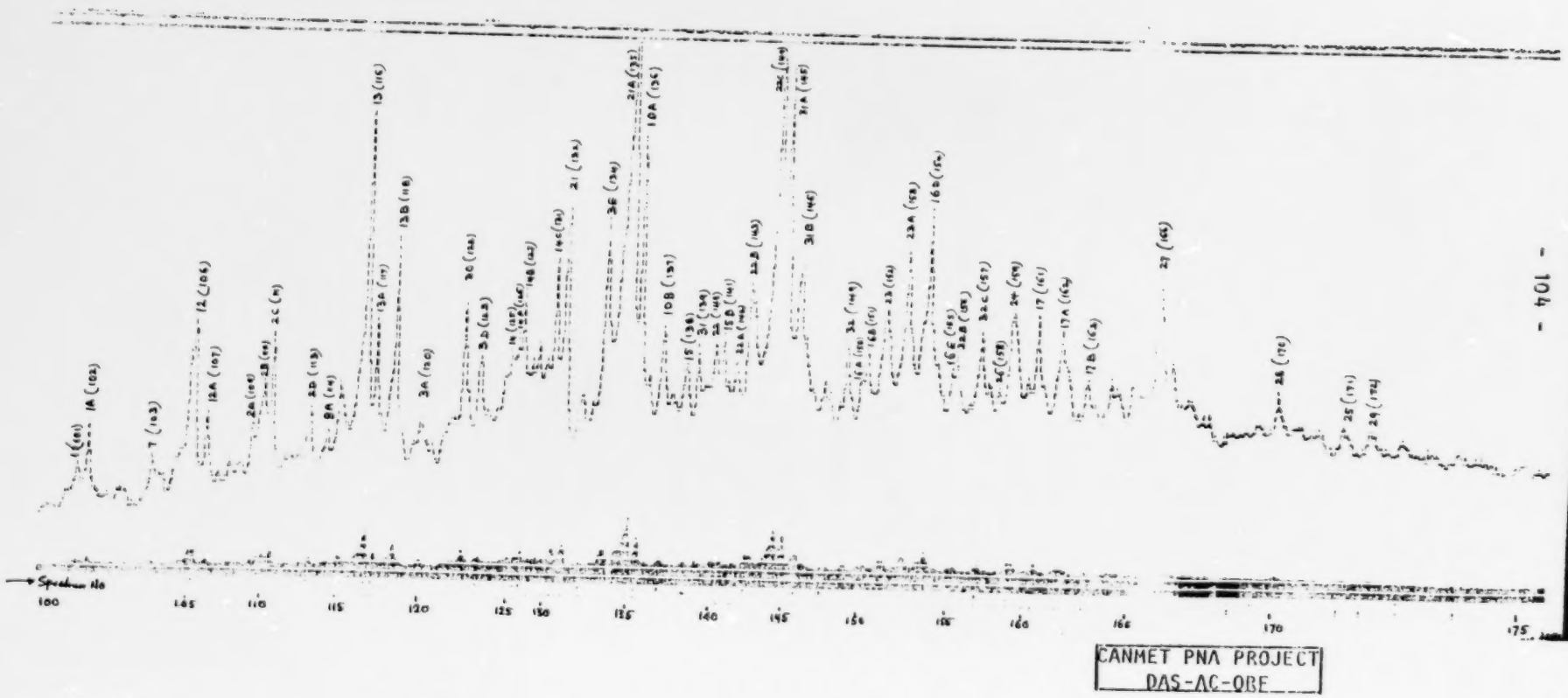

Figure 41. Capillary GC-MS Chromatogram of CANMET Sample # 4 (Expt 14)
(Conditions as in Figure 37)

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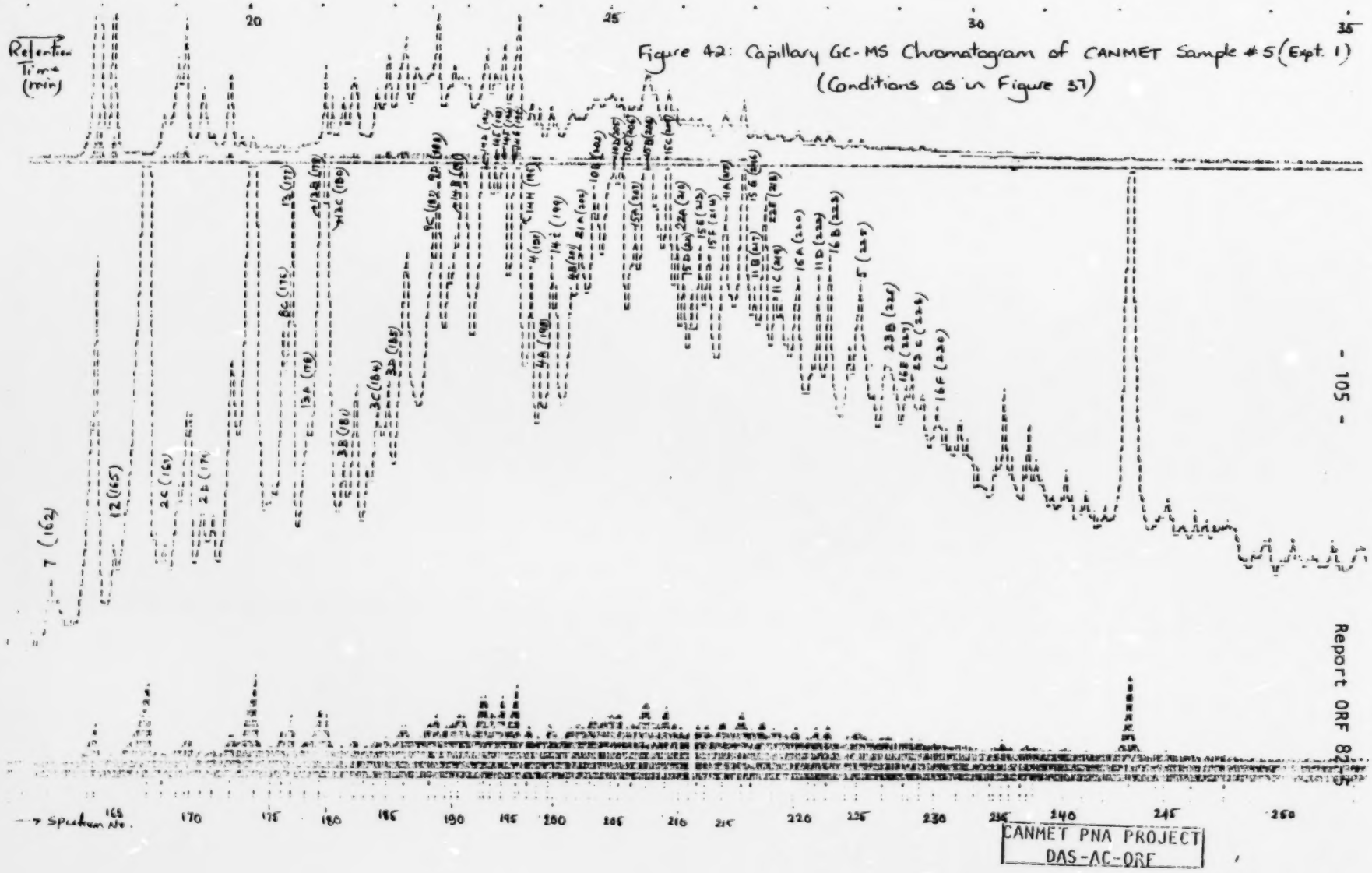

Figure 42: Capillary GC-MS Chromatogram of CANMET Sample #5 (Expt. 1)
(Conditions as in Figure 37)

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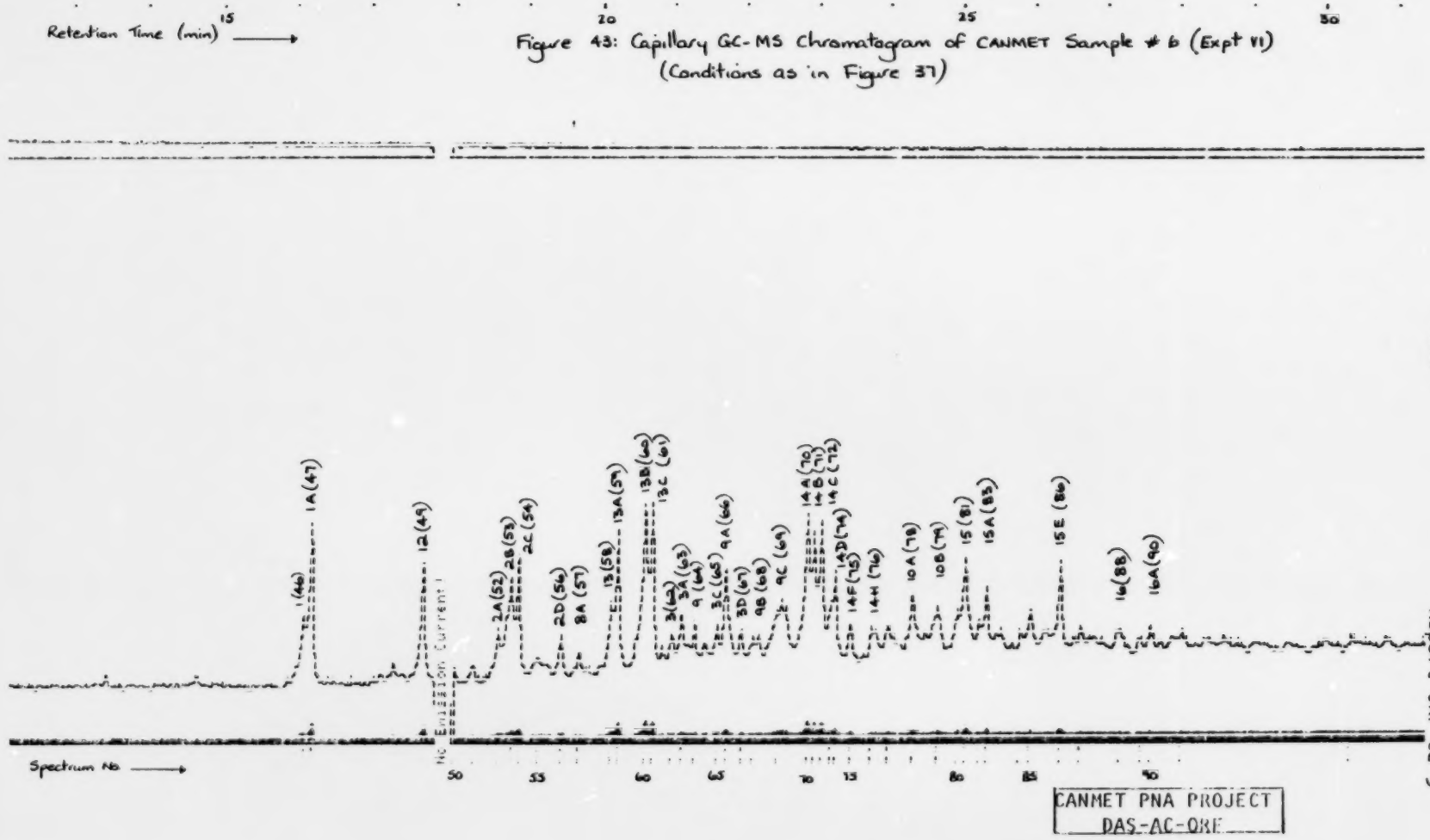

Figure 43: Capillary GC-MS Chromatogram of CANMET Sample # 6 (Expt VI)
(Conditions as in Figure 37)

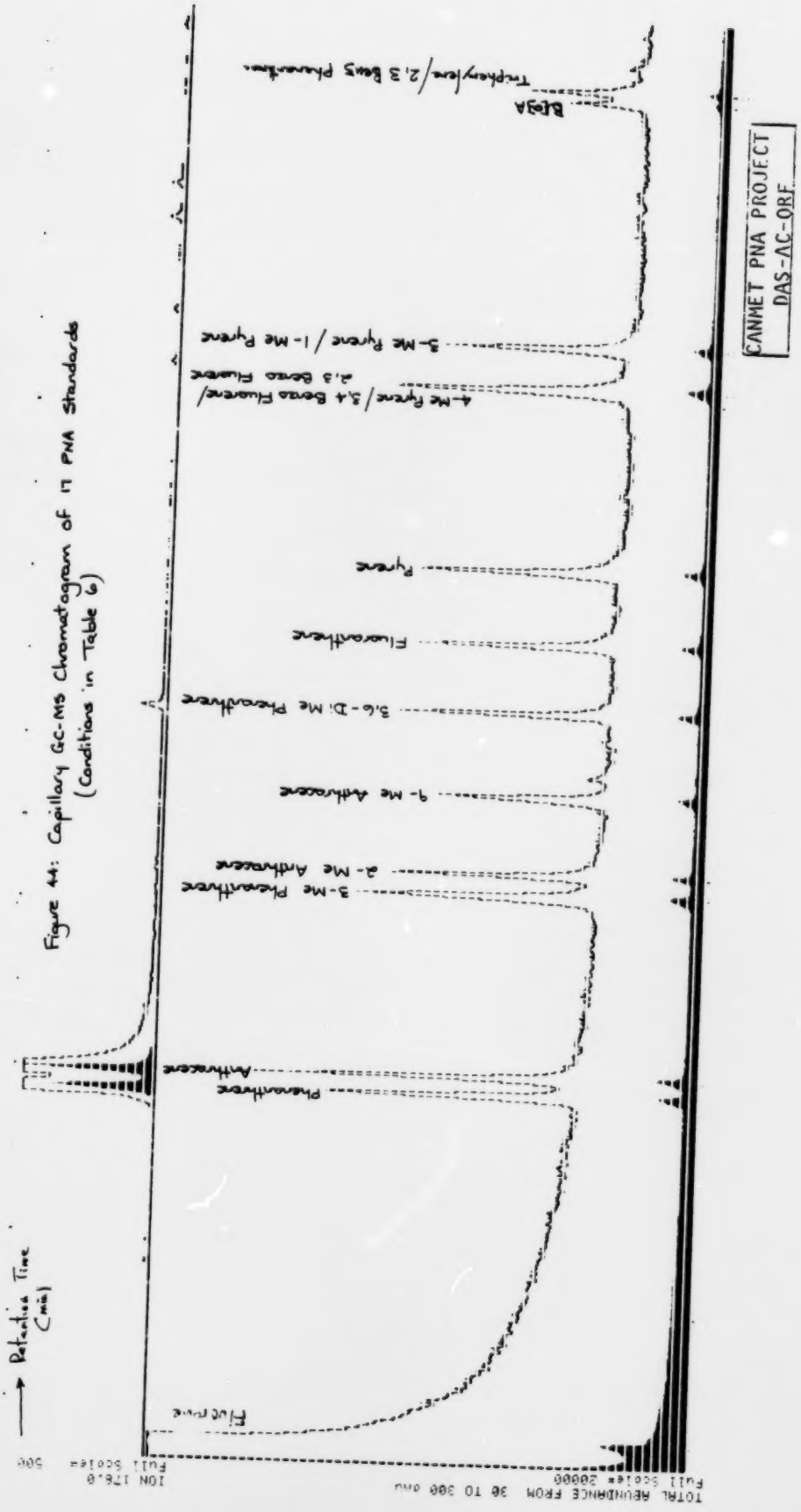

Figure 44: Capillary GC-MS Chromatogram of 17 PNA Standards
(Conditions in Table 6)

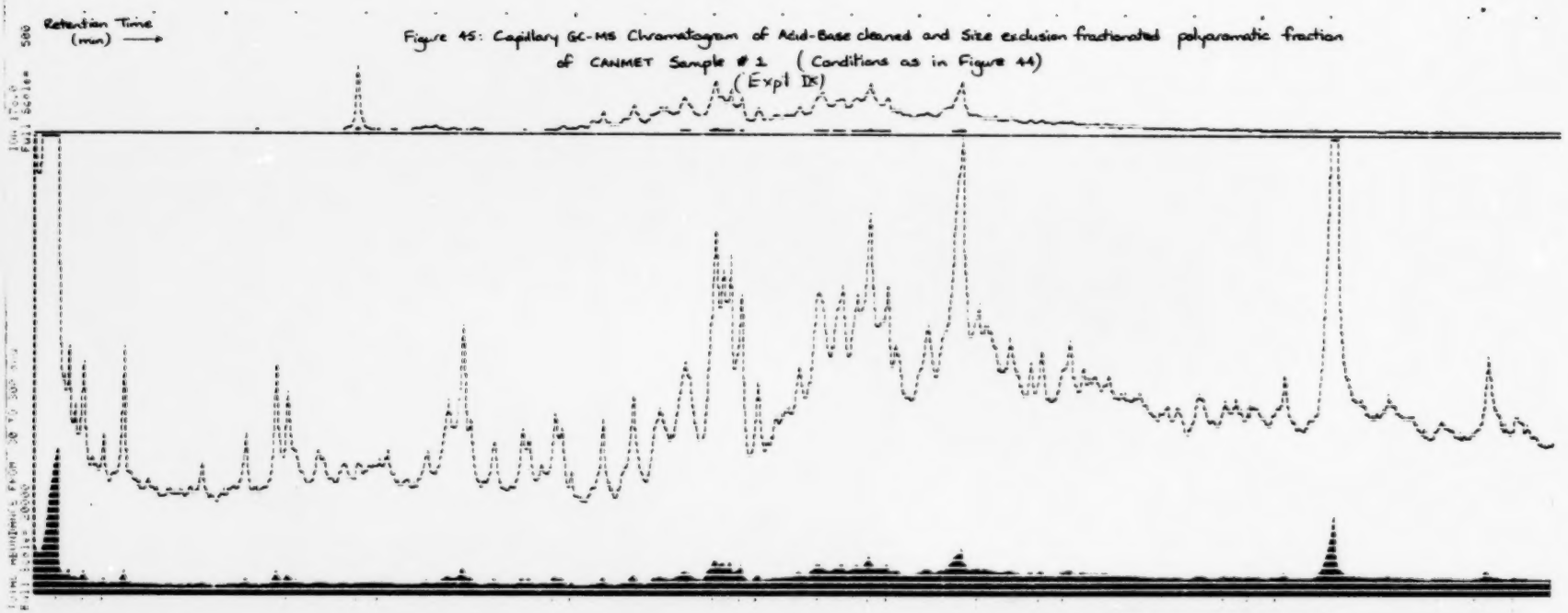

Figure 45: Capillary GC-MS Chromatogram of Acid-Base cleaned and Size exclusion fractionated polyaromatic fraction of CANMET Sample # 1 (Conditions as in Figure 44) (Expt IX)

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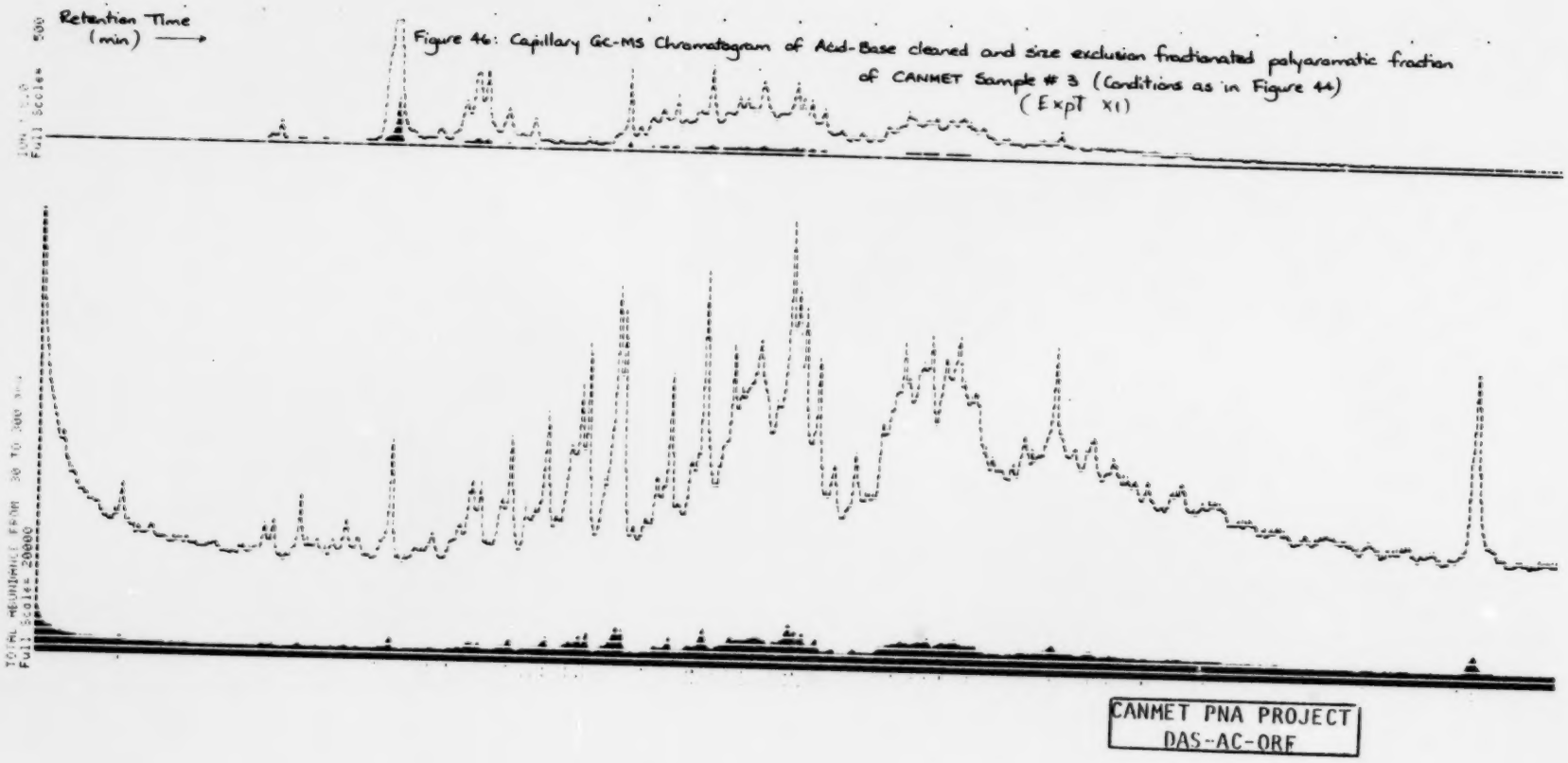

Figure 46: Capillary GC-MS Chromatogram of Acid-Base cleared and size exclusion fractionated polyaromatic fraction of CANMET Sample # 3 (Conditions as in Figure 44) (Expt X1)

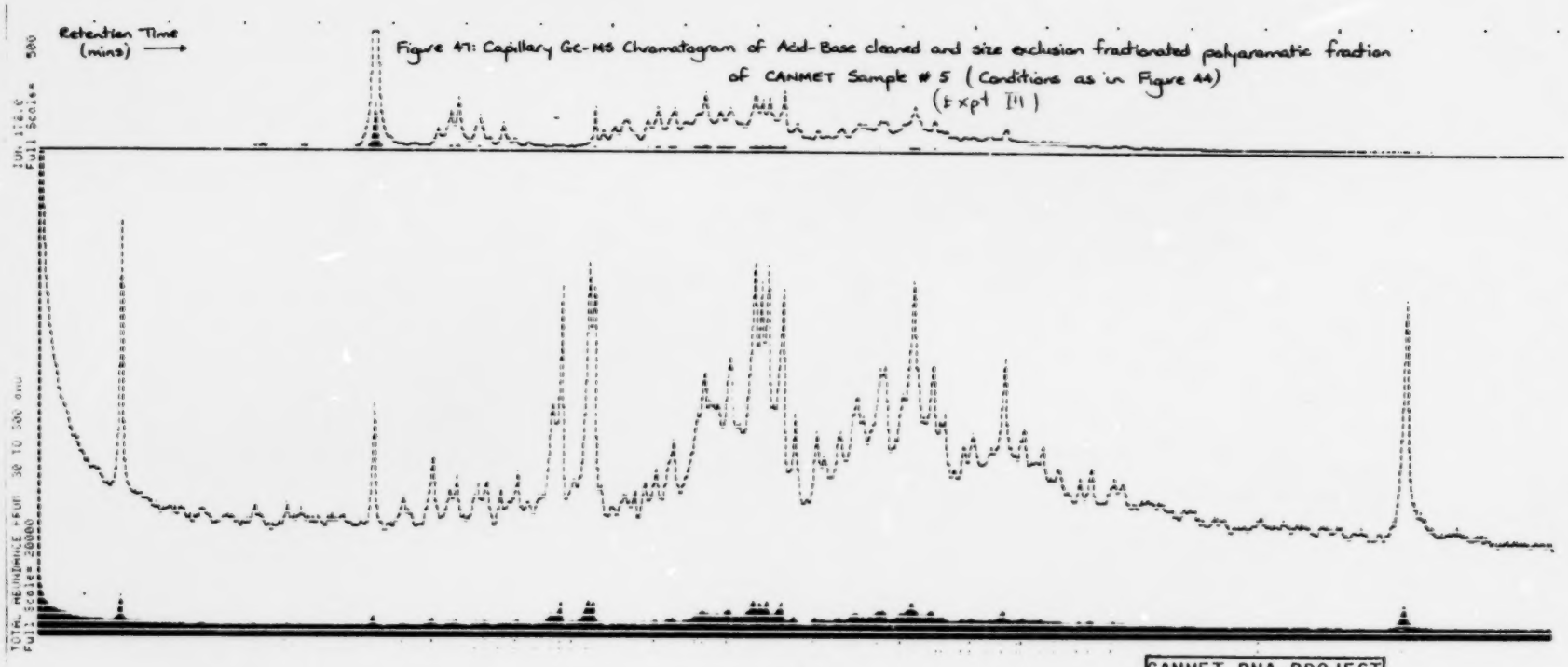

Figure 47: Capillary GC-MS Chromatogram of Acid-Base cleaned and size exclusion fractionated polyaromatic fraction of CANMET Sample # 5 (Conditions as in Figure 44) (Expt 111)

CANMET PNA PROJECT
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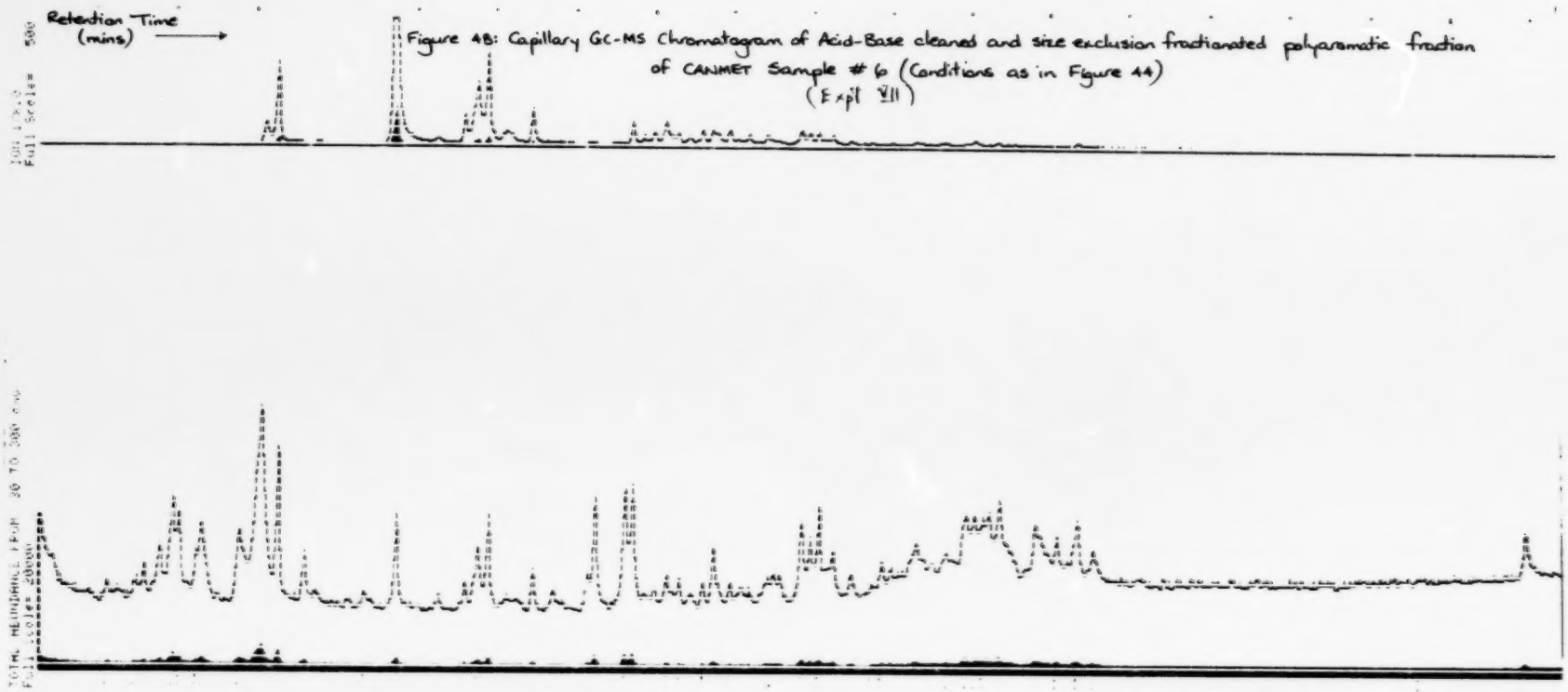

Figure 48: Capillary GC-MS Chromatogram of Acid-Base cleaned and size exclusion fractionated polyaromatic fraction of CANMET Sample # 6 (Conditions as in Figure 44)
(Expt VII)

POOR

QUALITY

ORIGINAL